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ON THE OXIDATION OF *d*-GLUCOSE IN ALKALINE SOLUTION BY AIR AS WELL AS BY HYDROGEN PEROXIDE

BY J. W. E. GLATTFELD

The oxidation of *d*-glucose in approximately half normal potassium hydroxide solution (9 molecules) by means of hydrogen peroxide has been studied in this laboratory by Spoehr,[1] who found that four oxidation products—namely, small amounts of carbon dioxide (3.51 per cent.), glycollic acid and a new hexonic acid, $C_6H_{12}O_7$, α-hydroxymethyl-*d*-arabonic acid, besides very large amounts of formic acid (65.3 per cent.)—are formed.

Preliminary experiments by Nef had convinced him that Spoehr, in carrying out the very difficult separations by means of alkaloidal salts, must have overlooked the presence of *dl*-glyceric acid and of isomeric trihydroxybutyric acids which are also formed in this oxidation process; and since, furthermore, Nef has recently succeeded in finding a perfectly general method for oxidizing all sugars in very dilute alkaline solutions at low temperatures (40°) with air *without the simultaneous formation of saccharinic acids*, it was now possible to show also by experiment that *d*-glucose, when oxidized in alkaline

[1] THIS JOURNAL, **43**, 233–245.

solution by air, gives exactly the same oxidation products as when hydrogen peroxide is used. The problem therefore assigned to me by Dr. Nef was to determine especially the nature of all the nonvolatile hydroxy acids formed from *d*-glucose in alkaline solution by air as well as by hydrogen peroxide.

The new hexonic acid considered by Spoehr to be α-hydroxymethyl-*d*-arabonic acid, HOOC–CH(OH)–CH(OH)–CH(OH)–CH(OH)–CH_2OH,

was obtained by him in the form of a thick viscous lactone gum possessing a specific rotation of 72°.5, and he had apparently established its constitution as named by an analysis of its well-crystallized calcium salt, and of its phenylhydrazide, as well as by its oxidation, with loss of carbon dioxide, to *d*-trihydroxyglutaric acid, HOOC–CH(OH)–CH(OH)–CH(OH)–COOH.

I succeeded in obtaining Spoehr's acid in the form of its crystallized γ-lactone melting at 96°–98° and have made an exhaustive study of its crystalline derivatives; it finally became perfectly apparent that the acid was not a new hexonic acid but a pentonic acid identical with Ruff's *d*-arabonic acid,

HOOC–CH(OH)–CH(OH)–CH(OH)–CH_2OH.

In an exactly similar way Dr. Nef has recently proved that Lucas' so-called new α-hydroxymethyl-*d*-lyxonic lactone,[1] which is obtained in large quantities by oxidizing *d*-galactose in dilute sodium hydroxide solution by air, is identical with the γ-lactone of *d*-lyxonic acid, HOOC–CH(OH)–CH(OH)–CH(OH)–CH_2OH,

i. e., an optically active pentonic acid is formed.

[1] Ann. Chem. (Liebig), **376**, 55, footnote.

We have therefore here at last the proof sought for for over nine years past by Nef[1] that all hexose sugars in the form of 1,2-hexosedienols,

$$HOCH = C(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).\overset{*}{C}H_2OH,$$

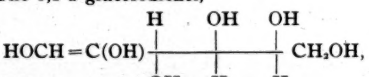
dissociate into hydroxymethylene and various methylenenols of pentose sugars; and since previous experiments by Nef prove very sharply that hexose sugars in the form of 2,3-hexosedienols,

$$HOCH_2.C(OH) = C(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).CH_2OH,$$

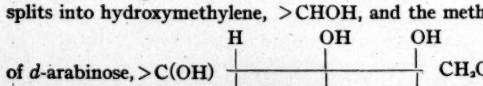
and 3,4-hexosedienols,

$$HOCH_2.\overset{*}{C}H(OH).C(OH) = C(OH).\overset{*}{C}H(OH).CH_2OH,$$

dissociate into diose and isomeric tetrose sugars as well as into two molecules of glyceraldehydemethylenenol, it is now certain that every hexose sugar in alkaline hydroxide medium, besides giving a mixture of six sugars of the corresponding series,[2] splits spontaneously into a mixture of various sugars containing one, two, three, four and five carbon atoms, $(CH_2O)_x$. The 1,2-*d*-glucosedienol,



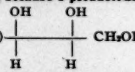
common to *d*-glucose, *d*-mannose and *d*-fructose, obviously splits into hydroxymethylene, >CHOH, and the methylenenol



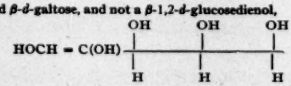
of *d*-arabinose, >C(OH)

[1] Ann. Chem. (Liebig), **357**, 259; **376**, 52.

[2] *d*-Allose and *d*-latose are *not* present as members of the *d*-glucose series [cf. *Ann.* Chem. (Liebig), **357**, 294; **376**, 87] because *d*-pseudofructose gives only a 2,3-*d*-glucosedienol, $HOCH_2.C(OH) = C(OH)$



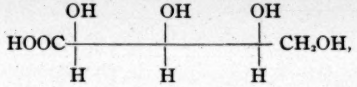
CH_2OH, common to it, *d*-fructose and *α*- and *β*-*d*-galtose, and not a *β*-1,2-*d*-glucosedienol,



CH_2OH.

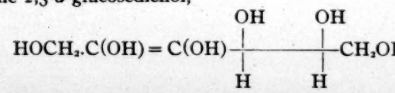
J. U. Nef.

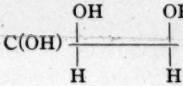
which then mainly takes up oxygen to give *d*-arabonic acid; at the same time it is very probable that some *d*-ribonic acid,

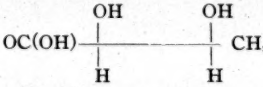


is also formed, but I was unable to establish this experimentally (see below).

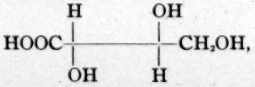
The 2,3-*d*-glucosedienol,



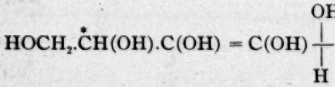
similarly splits into the methylenenols of diose, $HOCH_2.C(OH)<$, and of *d*-erythrose, $>C(OH)$  which should therefore take up oxygen to give *d*-erythronic acid,



This was in fact the *chief optically active trihydroxybutyric acid* found by me among the oxidation products of *d*-glucose with air as well as with hydrogen peroxide; at the same time a very small amount of optically active *l*-threonic acid,



is also unquestionably formed. The 3,4-*d*-glucosedienol,



obviously splits spontaneously as soon as formed into two molecules of glyceraldehydemethylenenol,

$$2HOCH_2.CH(OH).C(OH)<,$$

which naturally takes up oxygen to give *dl*-glyceric acid, hence this acid was found by me as an oxidation product under the conditions named. In addition, glycollic acid and especially large amounts of formic acid (65.2 per cent. and 14.8 per cent., respectively, with hydrogen peroxide and air) are obtained as oxidation products; these are formed mainly through the direct oxidation of hydroxymethylene, >CHOH, and of diosemethylenenol, $HOCH_2C(OH)<$.

Especially noteworthy is the fact that *none* of the six-carbon-atom sugars originally present in the alkaline solution—*d*-glucose, *d*-mannose, *d*-fructose, *d*-pseudofructose and α- and β-*d*-glutose (3-ketohexoses)—actually oxidize to their corresponding hexonic acids. This apparently only happens when Fehling's solution is used.[1] It is still possible that small quantities of *d*-mannonic and *d*-gluconic acids are formed when *d*-glucose (or any other of the six components of the *d*-glucose series) is oxidized in alkaline solution by air or hydrogen peroxide, but I was unable to establish their presence by experiment.

EXPERIMENTAL PART

I. The Action of Hydrogen Peroxide on d-*Glucose in Alkaline Solution*

In order to obtain as much nonvolatile hydroxy acid gum as possible, 75 grams of *d*-glucose were dissolved in two liters of cold three per cent. hydrogen peroxide and six equivalents of concentrated sodium hydroxide solution (102 grams of ninety-eight per cent. sodium hydroxide in 240 cc. water) were then slowly added in approximately equal portions, one equivalent immediately and the others at the end of 5, 9, 23, 27 and 32 hours, respectively. One hundred cc. more hydrogen peroxide were added at the end of 29 hours and when all the alkali had been introduced—at the end of 32 hours—465 cc. more hydrogen peroxide were added, so that the total volume of the solution rose to about three liters. The mixture was then allowed to stand 39 hours longer at ordinary temperature, when the test for sugar had become very faint, whereas the solution still gave—as throughout every stage in the oxidation process—a strong test for hydrogen peroxide.

[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 259–286.

Four such portions of seventy-five grams of *d*-glucose were worked up simultaneously, as well as another portion of 50 grams of *d*-glucose in 1500 cc. three per cent. hydrogen peroxide, to which, however, the six equivalents of sodium hydroxide in a small amount of cold water had been added in portions in the course of five days instead of 32 hours as in the other four cases.

At the end of seventy-one hours each of the four solutions was concentrated by distillation at 50° under 40 mm. pressure to about 800 cc. A test for sugar at this point showed none to be present. The solutions were then extracted twice with ether in order to remove small amounts of aniline formed by the hydrolysis of acetanilide which was present in very small amounts in the commercial hydrogen peroxide used. They were then acidified with concentrated hydrochloric acid. Twice the amount necessary to neutralize the alkali used was added. On distilling to a small volume at 60° under 30 mm. pressure, large amounts of sodium chloride had separated out. About two liters of 95 per cent. alcohol was now added to the mixture. The sodium chloride was filtered off and washed thoroughly with 95 per cent. alcohol. The filtrates were then distilled off completely at 60° under 30 mm. pressure and the residue was thoroughly extracted with absolute alcohol. At this stage the corresponding absolute alcohol extract obtained from the above-mentioned oxidation of 50 grams of *d*-glucose was combined with those obtained from 300 grams *d*-glucose as just stated, and the alcohol was then removed by distillation at 60° under 20 mm. pressure, giving thus a total of 83 grams crude brown nonvolatile gums, from 350 grams *d*-glucose, which still contained a very small amount of sodium chloride.

These gums were now resolved by two successive digestions with one liter of ethyl acetate into two soluble fractions:[1] 39 grams with $[\alpha]_D^{20}$ 33°.97 and 6.5 grams with $[\alpha]_D^{20}$ 47°.08, after freeing from ethyl acetate, etc., by sweeping over with water at 80° under 20 mm. pressure. These fractions were again united and extracted four times with one liter of ether

[1] All the optical determinations in the entire course of this work were made in approximately 4 per cent. aqueous solution.

and thus a total of 17.45 grams soluble gums, *A*, with $[\alpha]_D^{20}$ 23°.78, was obtained, leaving 25.5 grams gums, *B*, undissolved. The portion of the original 83 grams gums left undissolved by ethyl acetate was found to weigh 31 grams, gum *C*, with $[\alpha]_D^{20}$ 44°.35. Since *d*-arabonic acid gives a very difficultly soluble phenylhydrazide, and it was obviously not possible to separate the nonvolatile hydroxy acids to any appreciable degree by fractional solution in solvents, I decided to treat the gums *A*, *B* and *C* with phenylhydrazine. This was invariably done by mixing the gums with a volume each of phenylhydrazine and absolute alcohol equal to the weight of the gum taken, warming gently and stirring until a homogeneous mixture resulted. The crystalline hydrazide separated out completely in the course of 24 hours' standing at ordinary temperature, and was then filtered off and washed until snow-white with absolute alcohol. The gummy hydrazides left in the alcoholic filtrates were freed from alcohol by distillation under 20 mm. pressure in a bath kept at 40°–50°, and then freed from the excess of phenylhydrazine by threefold extraction in aqueous solution with ether. On removal of the water by distillation under reduced pressure, and dissolving the residue in eight parts of absolute alcohol, usually a fair amount more of crystalline hydrazide separated out. In this way I obtained from the above-mentioned three gums a total of 72.15 grams of acid hydrazides melting from 195° to 209°, as follows: Gum *A*, 17.45 grams, gave 8.8 grams crystals melting from 205° to 209°; Gum *B*, 25.5 grams, gave 25.95 grams crystals melting from 195°–204°; Gum *C*, 31 grams, gave 30.1 grams crystals melting from 195°–200°. The combined alcoholic filtrates, treated as stated above, gave 54 grams of gummy hydrazides which, dissolved in 400 cc. absolute alcohol, gave 7.3 grams more of crystals melting at 195°, and the gummy hydrazides left in the filtrate, 45 grams, hydrolyzed 7 hours on a boiling water bath with 45 grams barium hydroxide, 45 cc. water, etc. (see below), gave back 19 grams of nonvolatile hydroxy acids (see below) which were found to be optically inactive.

The Conversion of the Crude d-*Arabonic Phenylhydrazide into* γ-d-*Arabonic Lactone*

The 72.15 grams of crude *d*-arabonic phenylhydrazide obtained as just described were now hydrolyzed by heating 7 hours on a boiling water bath with 72 grams of crystallized barium hydroxide and 72 cc. water, taking care to shake from time to time. Much water was then added and the solution was filtered; the solids on the filter paper were then washed free of phenylhydrazine with ether and the filtrate also extracted five times with ether in order to remove the phenylhydrazine. The extracted solids and filtrate were then united and the barium precipitated in the usual manner, taking care to leave a trace of barium finally in the clear filtrate, which was then digested with charcoal. The crude *d*-arabonic lactone gum obtained after the customary removal of the water and extraction of the residue with absolute alcohol weighed 34 grams, $[\alpha]_D^{20}$ 60°.73, whereas the amount demanded by theory is 42 grams.

Nef has repeatedly emphasized[1] the fact that it is impossible to convert any polyatomic tetronic, pentonic or hexonic acid quantitatively into its γ-lactone. He has recently succeeded in isolating the pure β and γ monomolecular lactones of *d*-mannonic and *d*-gluconic acid.[2] *d*-Arabonic acid must therefore also give two lactones and this explains, in part at least, why I did not succeed in transforming the 34 grams of crude lactone gums quantitatively into the pure γ-lactone. Since, according to Nef's observations, the γ-lactone is invariably formed in larger ratio at higher temperatures, the method of procedure to obtain the γ-lactone is as follows: The crude lactone is first extracted with hot ethyl acetate and as much crystallized lactone is then obtained from the clear filtrate as possible by concentration, seeding, etc. As soon as the ethyl acetate solutions give no more crystals, the solvent is removed by distillation under reduced pressure and the residual β,γ-lactone mixture then heated in concentrated aqueous solution for 5 hours on a boiling water bath. The water is then removed

[1] Ann. Chem. (Liebig), **357**, 236.

[2] Soon to be published as a thesis by O. F. Hedenburg in THIS JOURNAL.

by distillation at high pressure and temperature, 80°–100°, and the gum then finally kept at 100° for some time under a pressure of 20 mm. This residue will then give more γ-lactone crystals with ethyl acetate, etc.

I succeeded in this way in obtaining a total of 23.18 grams crude γ-*d*-arabonic lactone crystals, which melted at about 96°, from the above-mentioned 34 grams of crude lactone mixture; and in addition 9 grams of gummy lactones, $[\alpha]_D^{20}$ 52.08°, were obtained from the ethyl acetate filtrates which were treated with brucine as described further on.

Pure γ-d-*Arabonic Lactone.*—On decolorizing with animal charcoal the aqueous solution of 11 grams crude γ-*d*-arabonic lactone crystals which consisted in part of the 23.18 grams mentioned above and in part of the 4.49 grams of similar γ-*d*-arabonic lactone crystals obtained in the air experiment, distilling the solution at 100° under 20 mm. pressure, taking up the residual gum in ethyl acetate and concentrating this solution under reduced pressure, I obtained in all 8.23 grams of beautiful, transparent, hard, measurable crystals melting at 96° to 98°. Ruff[1] gives the melting point of *d*-arabonic lactone as 97°–98° and its specific rotation as 73°.73 (in 10 per cent. concentration). Since it was not possible to determine by analysis whether a pentonic or a hexonic lactone was present, this was determined in favor of *d*-arabonic lactone by four independent titrations by two observers, Dr. Upson and myself, with 0.1 N alkali. Furthermore, I obtained a specific rotation of 68°.94 and 69°.68, respectively, for the crystals in four per cent. aqueous solution as follows:

(*a*) 0.6009 gram substance and 14.6303 grams water gave α in a 1 dcm. tube = 2°.75; and

(*b*) 0.4179 gram substance and 10.6952 grams water gave α in a 1 dcm. tube = 2°.65.

The analysis of 0.2149 gram substance gave 0.1054 gram H_2O and 0.3183 gram CO_2.

	Calculated for $C_5H_{10}O_5$	Found
C	40.54	40.40
H	5.40	5.49

[1] Ber. d. chem. Ges., **32**, 557.

Titration of the Lactone.—(1) 0.5298 gram lactone required 34.2 cc. 0.1 N sodium hydroxide for neutralization; the calculated value for $C_5H_8O_5$ is 35.8 cc. and for $C_6H_{10}O_6$, 29.78 cc.

(2) 0.4179 gram lactone required 26.3 cc. 0.1 N sodium hydroxide; calculated for C_5 lactone 28.24 cc. and for C_6 lactone 23.48 cc.

(3) 0.6009 gram lactone required 40.3 cc. 0.1 N sodium hydroxide; calculated for C_5 is 40.6 cc. and for C_6 is 33.76 cc.

(4) 0.603 gram lactone required 41.0 cc. 0.1 N sodium hydroxide (Upson); calculated for C_5 lactone is 40.75 cc. and for C_6 33.88 cc.

d-Arabonic lactone was therefore unquestionably present and this was further established by the analysis of the acid hydrazide and the calcium salt.

d-*Arabonic Phenylhydrazide.*—This compound was formed quantitatively by mixing 1 gram of pure lactone crystals with one volume each of phenylhydrazide and absolute alcohol. The crystals, which had separated out completely after 24 hours, were washed until snow-white with absolute alcohol and melted, after drying on a clay plate and *in vacuo* over sulphuric acid, between 213° and 214°. Ruff[1] gives the melting point of *d*-arabonic phenylhydrazide as 214°. The melting point of the antipode, *l*-arabonic phenylhydrazide, is likewise 214°, and its specific rotation in two per cent. aqueous solution has been determined by Nef as 14°.94, while Spoehr[2] gives —13°.9 as the specific rotation of the *d*-arabonic hydrazide in two per cent. aqueous solution. The analysis of my product shows very clearly that a pentonic and not a hexonic phenylhydrazide is at hand.

0.2852 gram substance gave 0.5384 gram CO_2 and 0.1612 gram H_2O.

0.2292 gram substance gave 22.4 cc. N_2 at 22°.3 C. under 729.9 mm. pressure.

	Calculated for $C_{11}H_{15}O_5N_3$	Calculated for $C_{12}H_{17}O_6N_3$	Found
C	51.54	50.35	51.49
H	6.30	6.29	6.32
N	10.94	9.79	10.86

[1] *Loc. cit.*

[2] This Journal, **43**, 240.

Calcium d-*Arabonate*, $(C_5H_9O_6)_2Ca.5H_2O$.—The crystallized calcium salt here studied was made from a gummy lactone obtained from crude *d*-arabonic brucine crystals (melting point, vacuum dried, 170°–176°) by hydrolysis. After the calcium determinations given below had been made the rest of this calcium salt—11.78 grams—was converted by the usual method into 6.56 grams gummy lactone; 5.29 grams of this gum gave with ethyl acetate, etc., 3.87 grams crystallized γ-*d*-arabonic lactone melting about 95° and with $[\alpha]_D^{20}$ 68°.65.

Three determinations of the calcium content of this salt were made. According to Ruff[1] this salt crystallizes with 5 molecules of water—the same is also true of its antipode—which cannot be removed *in vacuo* over sulphuric acid.

I. 0.2380 gram vacuum-dried salt gave 0.0292 gram CaO.
II. 0.2312 gram salt gave 0.0284 gram CaO.
III. 0.2730 gram salt gave 0.0338 gram CaO.

	Calculated for $(C_5H_{10}O_6)_2Ca.5H_2O$	Found I	Found II	Found III
Ca	8.71	8.77	8.78	8.85

The specific rotation of this salt, calculated for the anhydrous salt, was found to be, in agreement with Spoehr,[2] —3°.19 : 0.5656 gram salt dissolved in 13.4431 grams water gave α in a 1 dcm. tube = —0°.105, whence $[\alpha]_D^{20}$ for the hydrated salt is —2°.57 and for the anhydrous salt —3°.19.

Cinchonine d-*Arabonate*.—On heating an aqueous solution of 1 gram crude γ-lactone crystals for 4 hours on a boiling water bath with an excess of cinchonine, filtering off the undissolved alkaloid and distilling the clear solution at 70° under 20 mm. pressure, 2.50 grams of crude salt were obtained which required 30 cc. of hot absolute alcohol for solution. The clear filtrate deposited 1.08 grams of salt in the form of hard, radiating needles, melting between 178° and 180°, and possessing $[\alpha]_D^{20}$ 120°.3, *i. e.*, 0.405 gram salt and 9.9887 grams water gave α in a 1 dcm. tube = 4°.74.

Since Nef[3] has shown that cinchonine *l*-arabonate is a gummy

[1] *Loc. cit.*
[2] This Journal, **43**, 241.
[3] Ann. Chem. (Liebig), **357**, 227.

salt very soluble in cold absolute alcohol—an observation which I have confirmed—it is evident that *dl*-arabonic lactone can easily be resolved into its optical components by means of cinchonine. It follows also from this that the cinchonine *d*-gluconate obtained by Nef in his oxidation experiments with *d*-glucose, *d*-mannose, and *d*-fructose and Fehling's solution[1] must have contained cinchonine *d*-arabonate which—unlike its antipode—is also very difficultly soluble in absolute alcohol. Dr. Nef informs me that he feels certain that this was the case because the melting point of the cinchonine *d*-gluconate obtained by him in these experiments was not sharp (189°) but ranged from 170° to 187°. Furthermore, he noticed especially that on setting free the *d*-gluconic gum from this salt mixture he had great difficulty in obtaining sufficient crystallized calcium *d*-gluconate (even on seeding) for his optical determinations.

Strychnine d-*Arabonate*.—The crude lactone crystals, 1.03 grams, were digested in aqueous solution with an excess of strychnine until no more alkaloid dissolved and after removal of the water 3.28 grams of crude crystalline salt were obtained. This was practically insoluble in hot absolute alcohol but dissolved in a hot mixture of 9 cc. water and 60 cc. absolute alcohol. Fine feathery needles then separated out from the filtrate. They lost very little water on drying over sulphuric acid *in vacuo*, and weighed 2.3 grams after so drying. These crystals decomposed between 167° and 170° and gave $[\alpha]_D^{20} = -26°.08$, *i. e.*, 1.055 grams salt and 24.2331 grams water gave α in a 2 dcm. tube $= -2°.20$.

Quinine d-*Arabonate*.—This substance was made from 1.0 gram of the crude lactone crystals with the theoretical amount of quinine. The crude salt, 2.9 grams, dissolved in a hot solution of 3 cc. water and 30 cc. absolute alcohol, deposited a hard crust of indistinguishable crystals, 1.35 grams, melting from 172° to 173° and giving $[\alpha]_D^{20} -106°.2$; *i. e.*, 0.3589 gram substance and 8.7741 grams water gave α in a 1 dcm. tube $= -4°.22$.

Brucine d-*Arabonate*.—This especially characteristic salt of

[1] Ann. Chem. (Liebig), **357**, 267–270, 276, 281.

d-arabonic acid crystallizes from one-third its weight of water and three parts of alcohol in transparent plates melting from 167° to 170°; these lose 5.6 per cent. crystal water and become opaque on drying over sulphuric acid *in vacuo*, but the melting point remains unchanged. The specific rotation was found to be —26°.33, *i. e.*, 1.0555 grams salt and 25.3245 grams water gave α in a 2 dcm. tube = —2°.13. It is obvious from Spoehr's description of this salt[1] that it was at times contaminated with the high-melting (210°–220°) brucine salts of *dl*-glyceric, *d*-erythronic and *l*-threonic acids.

On the Constants of l-*Arabonic Lactone and its Derivatives.*— For the sake of comparison and to show more decisively, if possible, that the *d*-arabonic lactone obtained by me is the real antipode of the long-known *l*-arabonic lactone, I summarize here the various constants obtained by me and by other observers for *l*-arabonic lactone and its most characteristic derivatives. According to Nef's latest observations, 36.93 grams crude γ-*l*-arabonic lactone crystals give, when dissolved in 500 cc. hot acetone and filtered from a small amount of insoluble tar, by concentration to a small volume, 31.6 grams large, heavy, measurable, transparent crystals melting from 98° to 101° and possessing $[\alpha]_D^{20}$ —72°.2, *i. e.*, 0.4964 gram substance and 11.9138 grams water gave α in a 1 dcm. tube —2°.92. The specific rotation of the beautifully crystallized calcium salt, $(C_6H_9O_6)_2Ca.5H_2O$, is known to be 3°.1. I have made the brucine and strychnine salts of *l*-arabonic acid in the usual manner from 0.5 gram of Nef's purest γ-lactone (see above). The well-dried brucine salt melted at 160° and the strychnine salt at 117° (air dried) and 164° after drying *in vacuo*. Nef[2] gives the melting point of the vacuum-dried *l*-arabonic brucine as 155° and its specific rotation he has found to be —21°.74 (p = 4.0); the melting point of the air-dried strychnine salt was between 125° and 130°, and its specific rotation he has determined as —19°.1 (p = 4). The specific rotation of the phenylhydrazide has been determined by Nef as 14°.94 in two per cent. concentration (see above).

[1] THIS JOURNAL, **43**, 239.
[2] Nef: Ann. Chem. (Liebig), **357**, 227.

On the Unidentified Lactone Gums Obtained from the 72.15 Grams Crude d-*Arabonic Phenylhydrazide.*—As mentioned above, 9 grams of gummy lactones, $[\alpha]_D^{20}$ 52°.08, were obtained, besides 23.18 grams crude crystallized *d*-arabonic lactone, from 34 grams crude lactone gums. These were digested with 22 grams brucine, the heating being continued—as was customary—for one hour after the alkaloid had been dissolved. The cold aqueous solution was extracted three times with benzene and 35 grams of a crystalline residue obtained after removal of the water by distillation at reduced pressure. This residue, dissolved in a mixture of 10 cc. water and 160 cc. of absolute alcohol, deposited on standing 15.70 grams of crystals melting at 165° and possessing the characteristic appearance of *d*-arabonic brucine. The mother liquor then gave 15.7 grams crystalline brucine salts on distillation which, digested with 800 cc. absolute alcohol, left 0.95 gram insoluble salt melting at 195°. This may have been brucine *d*-mannonate, but I was unable to prove it by experiment. Furthermore, I was unable to establish the nature of the 14.75 grams salts dissolved by the 800 cc. absolute alcohol; I tried, for instance, to prove the presence of *d*-gluconic acid therein by conversion into the cinchonine salts, but without success. Since Nef has obtained small quantities of *l*-ribonic acid, as well as much *l*-arabonic acid, by the action of Fehling's solution on *l*-arabinose,[1] it is extremely probable that *d*-ribonic acid, which gives no well-defined alkaloid derivatives, was mainly present.

d-*Erythronic Lactone,* l-*Threonic Phenylhydrazide and* dl-*Glyceric Acid from the 19 Grams Optically Inactive Gums.*—The 19 grams inactive gums obtained by the hydrolysis of the 45 grams alcohol-soluble gummy hydrazides were digested in aqueous solution with 65 grams of brucine and then extracted as usual with benzene. Eighty-two grams of crystalline salts were left in the distilling flask after the removal of the water. These were dissolved in a hot mixture of 41 cc. water and 205 cc. of absolute alcohol and 15 grams of practically pure brucine *d*-erythronate melting at 209° separated out in plates on standing overnight. On crystallizing these from one-half a part of

[1] Ann. Chem. (Liebig), **357**, 231.

water and five parts of alcohol, 12.98 grams of thick crystal plates melting from 212° to 214° and possessing $[\alpha]_D^{20}$ —25°.62 separated out. Ruff gives $[\alpha]_D^{20}$ —23°.5 as the specific rotation of absolutely pure brucine *d*-erythronate.

γ-d-*Erythronic Lactone.*—On treating the 12.98 grams salts in aqueous solution with one and one-half times the calculated amount of hot aqueous barium hydroxide, filtering off the brucine and removing traces left in the alkaline solution by five-fold extraction with benzene, etc., 2.5 grams of lactone gum was obtained which solidified almost entirely on cooling. Since the sticky residue gave $[\alpha]_D^{20}$ —71°.0, practically pure γ-d-erythronic lactone must have been present. The substance was therefore dissolved in hot ethyl acetate and on concentration to a small volume, 1.82 grams of the pure lactone was obtained in colorless prisms melting from 102° to 103° and possessing $[\alpha]_D^{20}$ —73°.11, *i. e.*, 0.299 gram substance and 6.99 grams water gave α in a 1 dcm. tube = —3°.03. Ruff[1] gives —73°.3 as the specific rotation in 8 per cent. concentration and 103° as the melting point of this lactone. The amount of 0.1 N sodium hydroxide necessary for the neutralization of 0.4028 gram of this lactone was 33.3 cc. instead of 34.14, which is the amount demanded theoretically by $C_4H_6O_4$.

0.1792 gram of the lactone gave 0.0791 gram H_2O and 0.2661 gram CO_2.

	Calculated for $C_4H_6O_4$	Found
C	40.68	40.50
H	5.12	49.4

d-*Erythronic Phenylhydrazide.*—The 0.299 gram lactone used in the above-mentioned determination of specific rotation was treated in the customary manner with 0.3 cc. phenylhydrazide and alcohol. Owing to its great solubility only 0.3 gram phenylhydrazide melting from 119° to 120° was obtained. On crystallizing from a small amount of hot ethyl acetate 0.15 gram crystals melting at 125° and giving $[\alpha]_D^{20}$ 17°.10 was obtained, *i. e.*, 0.145 gram substance and 3.435 grams

[1] Ber. d. chem. Ges., **32**, 3679–80.

water gave α in a 0.5 dcm. tube = 0°.35. Ruff[1] gives the melting point as 128° and the specific rotation as 17°.5.

Strychnine d-*Erythronate*.—Recent experiments by Nef and myself have proved that *d*-erythronic and *l*-threonic acids give especially beautiful, well-crystallized and very difficultly alcohol-soluble salts; these, however, can not be used as a means of separating these acids from glycollic and *dl*-glyceric acids because of the formation of mixed crystals (see below).

Pure strychnine *d*-erythronate was made from 0.5 gram of pure *d*-erythronic lactone by digestion in aqueous solution with an excess of powdered strychnine. As the crude salt, 1.9 gram, was found to dissolve with the greatest difficulty in hot absolute alcohol, it was crystallized from 2 cc. water and 10 cc. absolute alcohol; there separated out on standing overnight 0.9 gram of radiating needles melting from 198° to 199° and possessing $[\alpha]_D^{20}$ —16°.84, *i. e.*, 0.2912 gram salt and 6.8933 grams water gave α in a 1 dcm. tube = —0°.69.

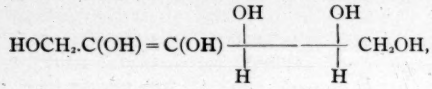
Quinine d-*Erythronate*.—The pure lactone, 0.5 gram, and the theoretical amount of quinine gave 1.95 grams crude salt. This, dissolved in 20 cc. hot absolute alcohol, gave a crop of long radiating hair-like needles weighing 0.8 gram and melting at 166° with $[\alpha]_D^{20}$ —106°.9; *i. e.*, 0.3384 gram salt and 7.9726 grams water gave α in a 1 dcm. tube = —44°.4.

l-*Threonic Phenylhydrazide*.—The alcoholic filtrate from the 15 grams crude brucine *d*-erythronate mentioned above still contained 61 grams brucine salts which, digested with 400 cc. absolute alcohol and allowed to stand overnight, yielded 29.6 grams insoluble salts melting at 197°. After several crystallizations of this fraction from one part water and ten parts absolute alcohol, 4.93 grams salts melting at 210° and possessing $[\alpha]_D^{20}$ —27.23° were obtained. These gave 0.9 gram lactone gum, $[\alpha]_D^{20}$ —33°.89, which yielded on the customary treatment with phenylhydrazine 0.37 gram (in two crops) crude *l*-threonic phenylhydrazide melting at 155° and giving $[\alpha]_D^{20}$ —25°.18. Since *l*-threonic phenylhydrazide, according to Anderson,[2] melts at 158°, crystallizes in transparent

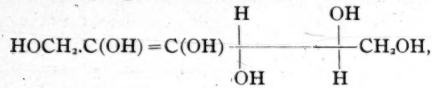
[1] *Loc. cit.*

[2] This Journal, **42**, 424.

plates and possesses $[\alpha]_D^{20}$ —31°.17 (Nef found $[\alpha]_D^{20}$ —28°.78 in two independent determinations), it is obvious that *l*-threonic acid is also an oxidation product of *d*-glucose by alkaline hydrogen peroxide, but it is formed in decidedly smaller amounts than its isomer, *d*-erythronic acid. In this connection it is interesting to note that *d*-galactose, when oxidized in alkaline solution by air, hydrogen peroxide, or Fehling's solution, gives, according to Nef's latest observations, relatively far larger amounts of *l*-threonic acid than of *d*-erythronic acid. This can be understood *only* on the assumption that the methylenenol of *d*-erythrose and *l*-threose which must be formed respectively by the dissociation of *2,3-d*-glucosedienol,



and of *2,3-d*-galactosedienol,



must in each case mainly take up oxygen directly, *i. e.*, before being transformed into ordinary *d*-erythrose and *l*-threose.

dl-*Glyceric Acid.*—On setting free the acids from the brucine salts still left in the alcoholic filtrates, 45 grams by actual determination, by means of barium hydroxide, etc., 9.0 grams of gum, $[\alpha]_D^{20}$ 16°.67, were recovered. This shows very clearly that a large amount of *d*-arabonic acid must still have been present in the above-mentioned 19 grams of inactive gums obtained from the hydrolysis of the gummy alcohol-soluble phenylhydrazide. The 9 grams of gum were accordingly extracted with half a liter of hot ether and a resolution into 1.86 grams soluble gum, $[\alpha]_D^{20}$ 3°.76, and 6 grams insoluble gum, $[\alpha]_D^{20}$ 21°.66, was thereby effected. The usual treatment of the 6 grams gum with phenylhydrazine removed 1.25 grams *d*-arabonic phenylhydrazide, melting at 195° to 200°. Hydrolysis of the alcohol-soluble hydrazides—including those obtained in treating the above-mentioned 0.9 gram crude

l-threonic gum, $[\alpha]_D^{20}$ —33°.89, with phenylhydrazine—gave back 3.96 grams acid gums, $[\alpha]_D^{20}$ 2°.5, which were therefore combined with the 1.86 grams of above-mentioned ether-soluble gums. These gave with brucine, etc., a total of 6.33 grams of high-melting (209°–214°) brucine salts which on hydrolysis gave 1.35 grams gum, $[\alpha]_D^{20}$ —10°.6. The C_4 gums—mainly *d*-erythronic—present in this gum were now removed by conversion into strychnine salts; 0.55 gram salts melting at 190° separated out on seeding and long standing. The alcoholic filtrate then gave back by barium hydroxide, etc., 1.25 grams gum, $[\alpha]_D^{20}$ 4°.4. The acid gums obtained from the 6.33 grams high-melting brucine salts by means of barium hydroxide, etc., weighed 2.77 grams and gave $[\alpha]_D^{20}$ 13°.7. Various attempts were made to resolve this gummy mixture by means of solvents (ethyl acetate) and alkaloids (strychnine) but without success, so that finally the recovered gums, about 1.75 grams, were united with the 1.25 grams gum, $[\alpha]_D^{20}$ 4°.4, which had given high-melting brucine salts (see above). The presence of a fair amount of *dl*-glyceric acid in this mixture was now unquestionably established by conversion of the combined gum, 3 grams, by digestion with quinine, subsequent extraction of the aqueous solution with ether to remove excess of alkaloid, and crystallization of the salts obtained, 12.15 grams, from water. A total of 3.7 grams of the very difficultly water-soluble quinine[1] *l*-glycerate, melting at 176°, separated out (in two crops) from the aqueous solution on standing. Over half of the total quinine salts obtained must therefore have consisted of quinine *dl*-glycerate.

II. On the Oxidation of d-*Glucose in Alkaline Solution by Air*

Fifty grams of *d*-glucose in a small amount of water were added to a cold solution of 68 grams of 98 per cent. sodium hydroxide (six equivalents) in 5 liters of water. A rapid stream of air was at once started through the solution by means of four tubes, each drawn out into six capillaries arranged in a starfish form. This enabled the air bubbles—which were first drawn through two sets of two concentrated aqueous potas-

[1] THIS JOURNAL, **48**, 421.

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sium hydroxide solutions connected by two Y-tubes with the four entrance tubes—to become scattered through the whole solution. Two powerful water pumps were necessary and the air stream was continued night and day for 46 hours. The temperature of the large water bath surrounding the round-bottom six-liter flask containing the sugar solution varied between 30° and 40°. No trace of sugar was found in the perfectly colorless alkaline solution at the end of the experiment. The exact amount of hydrogen chloride necessary to neutralize the sodium hydroxide used was now added and the water and formic acid were then removed by distillation under 20 mm. pressure, taking care to sweep over all the formic acid by redissolving in water, etc.

Determination of the Formic Acid.—The total amount of aqueous distillate, giving a barely perceptible opalescence with silver nitrate, was 5355 cc. One hundred cc. of this required 46.1 cc. 0.0999 N potassium hydroxide for neutralization (phenolphthalein), which is equivalent to 0.2118 gram formic acid; hence the total amount of formic acid formed from 50 grams *d*-glucose was 11.35 grams (14.8 per cent.).

The Nonvolatile Gummy Acids.—The residue in the distilling flask was now treated in aqueous solution with 160 cc. concentrated (36 per cent.) hydrochloric acid in order to insure the complete liberation of all organic acids. The residual gums, smelling therefore strongly of hydrochloric acid, were freed from sodium chloride in the usual manner; 36 grams of lactone gums, giving $[\alpha]_D^{20}$ 22°.98, and still containing small amounts of sodium chloride, were finally obtained, which shows that the yield of nonvolatile hydroxy acids is enormous when compared with the corresponding experiment with hydrogen peroxide. The gum was now resolved by digestion with half a liter of ethyl acetate into a soluble fraction, 26 g.; and an insoluble portion which, when freed from a small amount of sodium chloride by means of absolute alcohol, weighed 11 grams—gum *C*—and gave $[\alpha]_D^{20}$ 34°.27.

The soluble fraction was further resolved by thorough extraction with ether—four times with a half liter each time—into 12.8 grams ether-soluble gums, *A*, with $[\alpha]_D^{20}$ 10°.70,

and into 12.2 grams ether-insoluble gums, *B*, with $[\alpha]_D^{20}$ 36°.48. Gums *B* and *C* were now treated in the usual manner with phenylhydrazine and absolute alcohol; the former gave 8.25 grams phenylhydrazides melting at 210° and the latter gave 5.7 grams of similar crystals melting at 193°. These two crops were therefore united and worked up for *d*-arabonic lactone after adding 1.9 grams hydrazides, melting at 195°, subsequently obtained from the combined alcoholic filtrates by distilling off the alcohol *in vacuo*, dissolving in water, extracting with ether, etc. The gummy alcohol-soluble phenylhydrazides, 18 grams, then gave back on the usual hydrolysis with barium hydroxide, etc., 10 grams lactone gums, $[\alpha]_D^{20}$ 5°.75.

γ-d-*Arabonic Lactone.*—Hydrolysis of the combined high melting phenylhydrazides, 15.85 grams, by barium hydroxide now gave 8.0 grams of crude *d*-arabonic lactone gums. I succeeded in obtaining from these by extraction with ethyl acetate, digestion with water, etc., as described in Part I, 4.49 grams of crystallized γ-*d*-arabonic lactone giving $[\alpha]_D^{20}$ 67°.70, *i. e.*, 0.6093 gram lactone and 14.5007 gram water gave α in a 1 dcm. tube = 2°.76.

The total amount of the noncrystallizable lactone gums found in the filtrates was 3.0 grams; from these I obtained by conversion into brucine salts and subsequent crystallization only 3.3 grams of transparent crystalline plates melting from 167° to 170° and obviously consisting of brucine *d*-arabonate. It is, however, possible in this case also that a small amount of *d*-mannonic as well as of *d*-gluconic acid, and especially also some *d*-ribonic acid, was present, but I was unable to prove this by experiment.

d-*Erythronic Lactone and* dl-*Glyceric Acid.*—The *A* gums, 12.8 grams, $[\alpha]_D^{20}$ 10°.7, and the 10 grams gums $[\alpha]_D^{20}$ 5°.75, obtained from the alcohol-soluble gummy hydrazides from the *B* and *C* gums, obviously still contained a fair amount of *d*-arabonic lactone. I found first that it was possible to effect a considerable resolution of this gummy mixture by dissolving the gums partially in ten parts of hot acetic ester and then extracting the soluble portion with one hundred parts of hot ether. The ten-gram portion, for instance, was thus resolved into

three fractions: 3.0 grams, $[\alpha]_D^{20}$ —1°.6; 1.5 grams, $[\alpha]_D^{20}$ 6°.0; and 5.0 grams, $[\alpha]_D^{20}$ 11°.2, arranged in the order of solubility. Similarly, 9.5 grams of gum, $[\alpha]_D^{20}$ 10°.5, was resolved by digestion with half a liter of ether into 1.5 grams optically inactive soluble gums, and into 6.5 grams insoluble gums, $[\alpha]_D^{20}$ 18°.49; the latter then gave with phenylhydrazine 1.35 grams more *d*-arabonic phenylhydrazide, melting at 195° to 210°. Furthermore, I also tried conversion of the various gums into brucine salts in the hope of being able to accomplish a sharp separation of the high-melting (210° to 220°) brucine salts of *d*-erythronic, *dl*-glyceric and *l*-threonic acids from brucine *d*-arabonate which melts at 167° to 170°. I was unsuccessful in this, as I obtained large amounts of mixed crystals of these various salts, melting in the neighborhood of 180° to 200°. It was therefore with very great difficulty, and after many recrystallizations, that I finally obtained from the above-mentioned 22.8 grams of unidentified gums a total of 9.87 grams crude brucine *d*-arabonate melting from 150° to 170°, and 21.29 grams brucine salts melting from 208° to 214°. The latter then gave on treatment with barium hydroxide 4.15 grams lactone gum, $[\alpha]_D^{20}$ —10°.0, which on treatment with excess of strychnine took up 10.35 grams of this alkaloid. On distilling there was obtained a crystalline residue weighing 16 grams which gave two crops of salts on crystallization from spirit; 2.86 grams melting at 180° to 198°, with $[\alpha]_D^{20}$ —19°.43, and 2.38 grams melting at 130° to 150°, with $[\alpha]_D^{20}$ —18°.85. The former gave 0.8 gram lactone, $[\alpha]_D^{20}$ —44°.37, and the latter gave 0.57 gram gum, $[\alpha]_D^{20}$ 1°.7, which shows therefore the presence of small amounts of *d*-arabonic lactone.

The 0.8 gram gum, $[\alpha]_D^{20}$ —44°.37, solidified on cooling and gave, on crystallizing from a small amount of ethyl acetate, 0.3 gram of crude *d*-erythronic lactone, melting at 95°, and possessing $[\alpha]_D^{20}$ —66°.79, *i. e.*, 0.1085 gram lactone and 3.0495 grams water gave α in a 0.5 dcm. tube = —1°.16.

The 0.57 gram gum, $[\alpha]_D^{20}$ 1°.7, obtained from the second crop of strychnine salts, contained *dl*-glyceric acid mainly, for it gave on conversion into its quinine salt (1.74 grams obtained) a crop of 0.5 gram of quinine *l*-glycerate melting at 175° on crystallizing the salt from water.

Finally two other slightly active gums—2.95 grams, $[\alpha]_D^{20}$ 5°.7, and 2.33 grams, $[\alpha]_D^{20}$ 0°.86, the latter having been obtained from the alcohol-soluble strychnine salts from the above 4.15 grams lactone gum, $[\alpha]_D^{20}$ —10°.0—were converted into quinine salts. These gums took up 16 grams quinine and gave a crystalline residue of 25 grams. This residue gave on crystallization from water a total of 6.1 grams quinine *l*-glycerate melting at 174°, which proves very clearly that *dl*-glyceric acid was the main component of these gums. It is also clear from the above data that the separation of *dl*-glyceric acid from the two C_4 acids, *d*-erythronic and *l*-threonic, by means of strychnine, is not sharp but that mixed crystals of all of these components separate out from absolute alcohol. I have proved in an independent experiment that pure *dl*-glyceric acid gives with strychnine a low-melting (112° to 125°) crystalline salt which comes out to a very limited extent only from absolute alcohol, in which it is very soluble.

In conclusion, attention is drawn to the fact that I succeeded in proving definitely the nature of a far smaller proportion of the nonvolatile hydroxy acids formed by the action of air on an alkaline solution of *d*-glucose as compared with hydrogen peroxide. This is due mainly to the fact that in the former case relatively far greater amounts of *dl*-glyceric and optically active trihydroxybutyric acids are formed in proportion to the *d*-arabonic acid. I succeeded, for example, in obtaining only 17.75 grams of crude *d*-arabonic phenylhydrazide from 36 grams gums in the case of air, whereas I obtained 72.15 grams similar hydrazides from 83 grams of nonvolatile gums in the hydrogen peroxide experiment. The specific rotation of the original nonvolatile hydroxy acids was therefore also found to be far more strongly dextro in the latter case. Furthermore, experience has shown that it is impossible to remove more than a very small amount of *d*-arabonic lactone by the phenylhydrazine treatment of gummy mixtures whose specific rotation is not greater than 30°.0. It would therefore have been far more advantageous had I first resolved my gummy lactone mixtures, whose specific rotations varied from 5° to 30°, by digestion with solvents (small quantities of ethyl acetate

and subsequently much ether, etc.) into gummy fractions which were levorotatory and into dextrorotatory gums whose specific rotation was at least 40°, before further treatment with reagents.

To Dr. Nef, whose constant help alone made this work possible, I extend my heartiest thanks.

THE ACTION OF LIGHT ON ESTERS OF α-CYANOCINNAMYLIDENACETIC ACID. II

By Marie Reimer and Eleanor Keller

In a previous paper[1] it was shown that the action of light on the methyl and ethyl esters of α-cyanocinnamylidenacetic acid, exposed without solvent, is to cause polymerization of these compounds. This work has now been extended to a study of a number of esters of this acid with two purposes in view: To compare the reactions of the compounds when exposed to the light in the dry condition and in solution, and to obtain, if possible, geometrically isomeric esters and study their reactions.

In many cases substances containing an ethylene linkage, when exposed in solution to the light, are isomerized to an unstable form.[2] Exposed without solvent, the reaction is usually polymerization or oxidation or both. That the same substance may behave very differently according to conditions of exposure is shown in the case of cinnamic acid which, without solvent, is polymerized in the light to α-truxillic acid,[3] but, in solution in benzene, is isomerized to isocinnamic acid.[4] The behavior in the sunlight of α-cyanocinnamylidenacetic esters, also, has been found to depend on these conditions of exposure. The methyl, ethyl, propyl, isopropyl and isobutyl esters were investigated. Without solvent all of the esters polymerize to a dimeric form. This reaction is practically quantitative except in the case of the stable ethyl ester which is considerably oxidized. In solution in alcohol, polymeriza-

[1] This Journal, **45**, 417.
[2] Stoermer: Ber. d. chem. Ges., **42**, 4865; **44**, 637.
[3] Rüber: *Ibid.*, **38**, 2908.
[4] Stoermer: *Ibid.*, **44**, 666.

tion occurs in the case of the methyl ester only; all of the esters are decomposed slightly, oxidation taking place; and the ethyl ester is isomerized to an unstable form. In benzene solution the reactions are the same, except in the case of the methyl ester, which does not polymerize.

Of chief interest in the behavior of these esters is the fact that the geometrical isomers studied react differently on exposure to the light. Isomeric ethyl and isobutyl esters were prepared. The stable ethyl cyanocinnamylidenacetate, when exposed in the dry condition, is partially oxidized and partially polymerized, slowly, to form a dimeric product, melting at 166°, to which has been ascribed the formula

$$\begin{array}{l} C_6H_5CH : CCH : C(CN)COOC_2H_5 \\ \qquad\qquad\quad | \\ C_2H_5OOCC(CN) : CHCH_2CHC_6H_5 \end{array}$$

deduced from a study of the reactions of the compound as described in the previous paper. Exposed in solution in alcohol or benzene oxidation also occurs; more than 50 per cent. of the ester, however, is isomerized to an unstable form. The unstable ethyl cyanocinnamylidenacetate, exposed without solvent, is not oxidized but polymerized rapidly and quantitatively to the tetramethylene compound

$$\begin{array}{l} C_6H_5CH.CHCH : C(CN)COOC_2H_5 \\ \quad | \qquad\quad | \\ C_2H_5OOCC(CN) : CHCH.CHC_6H_5 \end{array}$$

melting at 128°, which was previously described.

In solution the unstable form is affected by light less rapidly than the stable form. The compound is oxidized slightly, but no isomerization could be detected.

Exposed without solvent, then, one of these esters is oxidized, the other is not; both polymerize to give products not identical but structurally isomeric. In solution the stable ester is isomerized to the unstable form but the reverse of this reaction has not been found to take place.

The differences between the reactions of the two isobutyl esters is not so marked. Without solvent, the stable ester polymerizes more rapidly than its isomer to form a stable tetramethylene compound, the structure of which is proved

by its oxidation to α-truxillic acid. The unstable ester polymerizes slowly to give a compound which breaks down rapidly in hot alcohol and which, on oxidation, gives a mixture of products from which no pure compound has been obtained. This polymer differs, therefore, in structure from that obtained from the stable form. Exposed to the light in solution, the unstable ester is decomposed more rapidly than the stable form. Neither ester has been found to isomerize.

Since the difference in the behavior of these isomeric esters is undoubtedly due to their difference in spatial configuration, it is quite probable that the action of light on other ethylenic compounds is determined, not only by the chemical influence of the groups present and the structure, but also, to a certain extent at least, by the spatial configuration of the molecule. The anomalous behavior of cinnamylidene compounds, on exposure, recently pointed out by Stobbe,[1] may find an explanation in the assumption that in this series compounds of different configuration, which, therefore, react differently in the light, are compared.

A satisfactory comparison, then, of the action of light on a series of unsaturated compounds can be made only when the conditions of the reactions are the same in all cases and when as many isomeric forms as possible have been investigated.

The behavior of the polymeric compounds formed from these esters, when exposed to the light in solution, has also been investigated for the purpose of testing Stewart's theory that the mechanism of the isomerization of unsaturated compounds in the light is the formation, from two molecules of the compound exposed, of a molecule of a tetramethylene polymer, which immediately breaks down in a different way from that in which it was formed to give two molecules of an isomeric form of the original compound.[2] The objection to this theory has been that tetramethylene compounds are not unstable and do not thus break down in solution. The polymeric compounds formed from the esters here described do, however, decompose in alcoholic solution when heated or when exposed to the light.

[1] Ber. d. chem. Ges., **45**, 3396.
[2] P. Chem. Soc. (London), **21**, 73.

The yellow solutions were found to contain, however, no isomeric form of the esters but only decomposition products. The polymer formed from the stable ethyl ester, which breaks down even more readily than the tetramethylene polymers, gives only decomposition products while the stable ethyl ester itself isomerizes to give a 60 per cent. yield of the unstable ester. Although these polymeric compounds are decomposed in solution there is, then, no evidence of the formation of isomers. A more plausible explanation of the isomerization reaction would seem to be that there is formed an intermediate addition compound, much less stable than any isolated, perhaps by some such reaction as that suggested by Emil Fischer to account for the Walden inversion,[1] which breaks down to give the unstable form of the original compound.

The action of light on other cinnamylidene esters is in progress in this laboratory.

EXPERIMENTAL

The finely powdered esters were exposed to the sunlight in ten-gram lots spread out over glass plates twelve inches square. The temperature of exposure varied from 28° to 35° C. When a solvent was used the saturated solution was exposed in Erlenmeyer flasks. No catalytic agent was used in any reaction.

Methyl α-Cyanocinnamylidenacetate.—The preparation of this ester and the rapid formation of the tetramethylene polymer when it is exposed without solvent to bright sunlight were described in the previous paper. Dissolved in methyl alcohol, the ester rapidly loses its yellow color, the white polymeric compound separating out after a few days. After two months' exposure more than one-half of the ester had separated out in polymeric form. The very pale yellow solution left, on evaporation, more of the polymer and a trace of yellow oil smelling of benzaldehyde. Oxidation had therefore taken place as well as polymerization. In benzene solution, after one month's exposure, no polymer was formed; a considerable quantity of oxidation product and the unchanged ester were left on evaporation of the solvent. Since no isomeric form of

[1] Ann. Chem. (Liebig), **381**, 123.

the ester was obtained by exposure in solution, attempts were made to obtain an isomer by preparation of the methyl ester from the stable ethyl ester according to the method of Pfannl.[1] Ten grams of ethyl ester were suspended in 100 grams of methyl alcohol, potassium methylate added, one molecule for each molecule of the ethyl ester used, and the mixture shaken until the ethyl ester had all gone into solution. Almost immediately a nearly quantitative yield of methyl ester separated from the alcoholic solution. It was identical with the ester prepared by the usual methods. The reaction was repeated several times under varying conditions of temperature and concentration, but always with the same results.

The tetramethylene polymer was dissolved in methyl alcohol and exposed to bright sunlight. After several weeks a faint yellow color appeared. This color did not increase appreciably after six months. The alcoholic solutions, after spontaneous evaporation, left a trace of yellow oil, due evidently to oxidation, as benzaldehyde was present. There was no monomeric ester in the solution.

Ethyl α-Cyanocinnamylidenacetate (*Stable Form*).—This ester, melting at 113°, may be prepared quantitatively from the acid by heating the latter with a 3 per cent. solution of hydrochloric acid in ethyl alcohol or by the Claisen condensation of ethyl cyanoacetate with cinnamic aldehyde. On exposure to the light in the dry condition, oxidation takes place and 50 per cent. of the ester is polymerized to the compound melting at 166°, as previously described. Exposed in solution in ethyl alcohol, oxidation and isomerization occur. Eight grams of ester were dissolved in one liter of absolute alcohol and exposed to sunlight for six weeks. The alcohol was then allowed to evaporate spontaneously. The product was a dark oil with a strong nutty odor, filled with long needle-shaped crystals. The mixture was washed several times with small quantities of cold alcohol until the oil was all dissolved. From this alcoholic solution two grams of the original stable ester gradually separated. The crystals not dissolved by the cold alcohol were dissolved in the least possible quantity of boiling alcohol.

[1] Monats. Chem., **31**, 301.

From this solution 5 grams of unstable ester separated. In solution in benzene the results are the same. In bright sunlight over 60 per cent. was isomerized in 4–5 weeks. In subdued light the oxidation proceeds more rapidly than the isomerization so that little or no isomer was obtained in cases where the solution was not exposed to the bright sunlight.

The polymeric product is readily decomposed in alcoholic solution. On warming, the solution becomes yellow and then red. In the sunlight the reaction is not so rapid. Two grams of the ester were suspended in 100 cc. of ethyl alcohol and exposed. After two days a faint yellow color was discernible, the color rapidly increasing until the solution was a brilliant yellow. After 8 weeks the yellow solution was poured off and the alcohol evaporated. The only crystalline product separating was a little of the original polymer. The yellow color was that of an oil, having a characteristic nutty odor, in which benzaldehyde was present. Even in the dark the alcoholic solution of the polymer is decomposed slightly to form this yellow oil. Three grams of the polymer were suspended in two liters of alcohol and allowed to stand 1 month in the dark. The alcoholic solution, which had become a bright yellow, was then poured into several liters of water and the whole extracted with ether. On evaporation, the ether deposited a small quantity of yellow oil and a white crystalline compound, which separated from hot alcohol in fine, soft, colorless needles, melting at 182°. The quantity of this substance obtained in repeated experiments was not enough for analysis. As it is colorless, it may be an isomeric form of the polymer melting at 166°, the monomeric esters having invariably a yellow color.

Exposed in benzene solution, the reaction in the sunlight is the same as with alcohol. In the dark and on boiling the solution was not changed. In chloroform the decomposition in the light is extremely slow and in ether no change takes place. In no case was there any evidence of an isomeric form of the original ethyl ester.

Ethyl α-Cyanocinnamylidenacetate (*Unstable Form*).—This ester, melting at 113°, was first prepared by the reaction of potassium ethylate on an ethyl alcohol solution of the methyl

ester, as described in the previous paper. It can be prepared more conveniently by exposure to the bright sunlight of the stable ester in alcoholic or benzene solution. The substance is very readily soluble in benzene, chloroform and acetone, fairly soluble in ether, insoluble in ligroin. It is much less soluble in methyl and ethyl alcohols than the stable form and can, therefore, be separated from the latter by fractional crystallization from alcohol. It separates from absolute alcohol in broad, flat, straw-colored needles, very different in appearance from the fine branching yellow needles of the stable ester.

Analysis:

0.1998 gram substance gave 0.5443 gram CO_2 and 0.1137 gram H_2O.

	Calculated for $C_{14}H_{13}O_2N$	Found
C	74.00	74.27
H	5.72	6.32

Exposed to the sunlight in the dry condition, the ester polymerizes rapidly and completely to the tetramethylene compound, melting at 128°, previously described.

In solution in alcohol exposure to the sunlight causes a little deeper yellow color to appear after a few days. This is evidently due to the formation of the oily decomposition product which was left, together with unchanged ester, on evaporation of the solvent. Although there is no evidence of isomerization of this ester, it is quite possible that such a reaction does take place, the stable ester thus formed being decomposed as rapidly as it is formed.

The tetramethylene polymer exposed to the sunlight in solution in alcohol is decomposed with extreme slowness. After exposure for 10 weeks a very faint yellow color was noticeable. The only products obtained from the solution were the unchanged polymer and the oily decomposition product.

Propyl Cyanocinnamylidenacetate.—The compound was prepared by the Claisen condensation of cinnamic aldehyde with propyl cyanoacetate; from a solution of cyanocinnamylidenacetic acid in propyl alcohol saturated with hydrochloric acid; and by dissolving ethyl α-cyanocinnamylidenacetate in propyl alcohol and treating with one molecule of potassium propylate.

The same ester, separating from propyl alcohol in long, flat, orange-yellow crystals, melting at 107°, was obtained in all cases. It is very readily soluble in acetone, benzene and chloroform, readily soluble in ether, very slightly soluble in ligroin. It is fairly soluble in cold methyl, ethyl and propyl alcohols, from concentrated hot solutions in which it crystallizes readily.

Analysis:

0.1990 gram substance gave 0.5429 gram CO_2 and 0.1158 gram H_2O.

	Calculated for $C_{15}H_{15}O_2N$	Found
C	74.69	74.40
H	6.22	6.53

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
51.25	0.1604	0°.034	240
51.25	0.4499	0°.093	246

Calculated for $C_{15}H_{15}O_2N$, 241

In diffused daylight the ester slowly loses color until a perfectly white product is formed. In bright sunlight the reaction is very rapid. In an hour the substance becomes a clear yellow, pasty mass which rapidly loses color, white crystals gradually separating. The paste contains no oxidation product, as a quantitative yield of polymer was obtained, but is evidently a mixture of the mono- and polymeric forms. When treated with cold alcohol the mass solidifies to a pure white compound which separates from boiling propyl alcohol in fine white needles melting at 107°–108°. It is very slightly soluble in cold alcohols, readily soluble in hot alcohols, benzene, acetone and chloroform, slightly soluble in ether, insoluble in ligroin.

Analysis:

0.2004 gram substance gave 0.5500 gram CO_2 and 0.1184 gram H_2O.

	Calculated for $C_{30}H_{30}O_4N_2$	Found
C	74.69	74.85
H	6.22	6.56

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
41.19	0.2610	0°.034	486
41.19	0.4418	0°.054	518
	Calculated for $C_{30}H_{30}O_4N_2$,		482

The structure of this dimeric compound was determined by oxidation. Two grams were dissolved in acetone, the solution cooled and potassium permanganate added as long as decolorizarion took place. The excess of oxidizing agent was then decolorized by sulphur dioxide, the oxides of manganese filtered out and extracted repeatedly with hot water. From the aqueous solution hydrochloric acid precipitated α-truxillic acid which melted at 274° when mixed with a sample of α-truxillic acid from another source. Benzoic and oxalic acids were obtained from the filtrate. These results prove the compound to be dipropyltetramethylenebismethylenecyanoacetate:

$$\begin{array}{l} C_6H_5CH.CHCH : C(CN)COOCH_2CH_2CH_3 \\ \quad\quad\quad\

0.2012 gram substance gave 0.5511 gram CO_2 and 0.1203 gram H_2O.

	Calculated for $C_{15}H_{15}O_2N$	Found
C	74.69	74.70
H	6.22	6.70

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
54.44	0.2265	0°.044	246
54.44	0.5443	0°.110	237

Calculated for $C_{15}H_{15}O_2N$, 241

On exposure to the sunlight without solvent the ester rapidly loses color and becomes pasty. After 4–5 days the whole is a clear, colorless mass which crumbles to a white solid on treatment with cold alcohol. This solid separates from hot alcohol in stiff needles, colorless after several recrystallizations, melting at 136°. The compound is not readily soluble in cold alcohols nor in boiling ether, readily soluble in boiling alcohols, chloroform and benzene, fairly soluble in acetone, insoluble in ligroin.

Analysis:

0.2234 gram substance gave 0.6137 gram CO_2 and 0.1281 gram H_2O.

	Calculated for $C_{30}H_{30}O_4N_2$	Found
C	74.69	74.87
H	6.22	6.37

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
49.59	0.2938	0°.033	470
49.59	0.5644	0°.062	481

Calculated for $C_{30}H_{30}O_4N$, 482

On oxidation in acetone solution with potassium permanganate the product was α-truxillic acid as in the case of the propyl ester. The compound is, therefore, diisopropyl tetramethylenebismethylenecyanoacetate:

$$C_6H_5CH.CHCH : C(CN)COOCH(CH_3)_2$$
$$(CH_3)_2CHOOCC(CN) : CHCH.CHC_6H_5$$

On exposure in solution in alcohol the monomeric ester is decomposed more rapidly than the propyl ester. After exposure for several months a considerable quantity of yellow oil, smelling strongly of benzaldehyde, was deposited from the solution, together with a small amount of unchanged ester. No isomer nor polymer was present.

The polymer in alcoholic solution very gradually breaks down on exposure to the light to give a pale yellow solution. The color here is due, as in the other reactions, to a small quantity of decomposition product which separates as a yellow oil on evaporation of the alcohol.

Isobutyl Cyanocinnamylidenacetate (*Stable Form*).—Ten grams of α-cyanocinnamylidenacetic acid were dissolved in 130 cc. of isobutyl alcohol saturated with hydrochloric acid and the mixture allowed to stand overnight. The crystalline product was then filtered and recrystallized from hot isobutyl alcohol. The substance separates in lemon-yellow plates, melting at 114°. It is fairly soluble in cold methyl, ethyl and isobutyl alcohols and ether, readily soluble in hot alcohols and acetone, very soluble in benzene and chloroform.

Analysis:

0.1979 gram substance gave 0.5468 gram CO_2 and 0.1245 gram H_2O.

	Calculated for $C_{16}H_{17}O_2N$	Found
C	75.29	75.35
H	6.66	7.05

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
46.04	0.1930	0°.043	254

Calculated for $C_{16}H_{17}O_2N$, 255

On exposure to sunlight the ester rapidly forms an oil from which colorless crystals begin to separate in 2–3 hours. If the light is very bright, but little of the oil is formed, the sub-

stance rapidly decolorizing to a white solid mass. After two days' exposure the product was crystallized from alsolute alcohol. It separates in brilliantly shining white needles, melting at 123°. The substance is readily soluble in acetone, benzene, chloroform and hot alcohols, very slightly soluble in boiling ether and ligroin.

Analysis:

0.2020 gram substance gave 0.5604 gram CO_2 and 0.1192 gram H_2O.

	Calculated for $C_{32}H_{34}O_4N_2$	Found
C	75.29	75.66
H	6.66	6.54

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
42.26	0.1884	0°.023	505

Calculated for $C_{32}H_{34}O_4N_2$, 510

On treatment in acetone solution with potassium permanganate, the compound is rapidly oxidized to give an almost quantitative yield of α-truxillic acid. The compound is, therefore, the tetramethylene polymer.

In solution in alcohol isobutyl cyanocinnamylidenacetate slowly decomposes on exposure. After one month the alcohol was allowed to evaporate off. A very small quantity of yellow oil, smelling strongly of benzaldehyde, was formed; the bulk of the ester crystallized out unchanged.

The polymer, dissolved in alcohol, also decomposed very slowly on exposure to give a pale yellow solution. An oil, having the characteristic nutty odor of the decomposition products already described, was the only substance isolated aside from the unchanged polymer.

Isobutyl α-Cyanocinnamylidenacetate (Unstable Form).—This ester was prepared by the Claisen condensation from cinnamic aldehyde and isobutyl cyanoacetate. It crystallizes from hot isobutyl alcohol in shining yellow plates melting at 110°–111°. It is readily soluble in hot alcohols, ether, chloroform, acetone and benzene, slightly soluble in ligroin.

Analysis:

0.1994 gram substance gave 0.5491 gram CO_2 and 0.1239 gram H_2O.

	Calculated for $C_{14}H_{17}O_2N$	Found
C	75.29	75.10
H	6.66	6.96

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
48.82	0.1802	0°.040	241
48.82	0.3963	0°.088	241

Calculated for $C_{16}H_{17}O_2N$, 255

The ester is isomeric with the one just described. On boiling in isobutyl alcohol saturated with hydrochloric acid it gradually changes to the higher-melting isomer. It may, therefore, be considered the unstable form. As the melting points of the two esters lie very close together and as they do not differ in appearance and but very slightly in solubility, they may most readily be distinguished by exposing small quantities of each to the light and comparing their behavior and the products formed. The unstable ester on exposure gradually forms a clear pasty product, readily soluble in the common organic solvents. After exposure for two weeks the paste has hardened to a clear mass which crumbles to a white powder when treated with cold alcohol. Crystallized from boiling absolute alcohol, the compound separates in fine white needles melting from 114°–115°. The alcohol solution from which the compound is crystallized becomes a dark, reddish yellow, showing considerable decomposition of the substance on heating in alcohol, as is the case with the polymer from the stable ethyl ester.

The substance is slightly soluble in cold alcohols, readily soluble in hot methyl, ethyl and isobutyl alcohols and in benzene, acetone and chloroform.

Analysis:

0.1886 gram substance gave 0.5194 gram CO_2 and 0.1180 gram H_2O.

	Calculated for $C_{32}H_{34}O_4N_2$	Found
C	75.29	75.18
H	6.66	6.41

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent	Gram substance	Rise in boiling point	Molecular weight
50.73	0.5658	0°.057	510
	Calculated for $C_{32}H_{34}O_4N_2$,		510

This substance is then a dimeric form of the unstable isobutyl ester, isomeric with the higher-melting polymer obtained by exposure of the stable isobutyl ester.

The oxidation of the two polymeric compounds was carried out side by side for purposes of comparison. Two grams of each polymer were dissolved in 50 cc. of acetone and treated slowly with 3 grams of potassium permanganate dissolved in 100 cc. of acetone. The mixtures were kept at 0° throughout the reaction. After complete decolorization of the permanganate the solutions were filtered and the oxides of manganese repeatedly extracted with boiling water. From the aqueous solution obtained by oxidation of the high-melting polymer hydrochloric acid precipitated an almost quantitative yield (1.0 gram) of α-truxillic acid as a pale yellow flocculent precipitate. From the aqueous solution obtained by oxidation of the low-melting polymer, hydrochloric acid precipitated about 0.1 gram of a pasty substance, which gradually solidified. After repeated crystallizations from alcohol this melted at 250°–270°. It behaved somewhat like α-truxillic acid but could not be identified as that acid. The aqueous solution filtered from this solid was extracted repeatedly with ether. On evaporation the ether deposited a solid which was crystallized from boiling water. It separates in white clumps melting at 210°–250° with decomposition. The substance is very soluble in the usual organic solvents. It has not yet been possible to obtain it in condition pure enough for analysis. It has none of the characteristics of the acid formed by oxidation of the polymer from the stable ethyl ester and, therefore, this unstable isobutyl polymer must differ in structure from any as yet obtained from these esters.

Exposed in solution in alcohol, the unstable isobutyl ester decomposes more readily than the stable ester. No isomeric nor polymeric form was found in the solution.

The polymeric product also decomposes more readily than that from the stable ester when exposed in alcoholic solution. Only the yellow oil, containing benzaldehyde, was isolated from the solution.

CHEMICAL LABORATORY
BARNARD COLLEGE
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REPORT

THE EVOLUTION OF AVOGADRO'S THEORY[1]

Avogadro put forward his celebrated hypothesis in 1811. In 1814 Ampère announced the same hypothesis. But it required more than half a century to bring chemists generally to its acceptance. Now it is a fundamental chemical and physical theory.

In 1804 Humboldt visited Berthollet and met Gay-Lussac who, though only 25 years old, had already distinguished himself, especially by the discovery of the law of expansion of gases. Humboldt, wishing to improve the method of analyzing air, invited Gay-Lussac to determine the best method of estimating oxygen in the air. It was necessary to determine accurately in what volumetric proportion oxygen unites with hydrogen. They found that 1 volume of oxygen combines with 2 volumes of hydrogen. They published the result in 1804. Later Gay-Lussac (1808) announced his law of volumes. He did not suggest any hypothesis by way of explanation.

Avogadro, in 1811, began his now-celebrated article by referring to the results of Gay-Lussac and then says:

"Il faut donc admettre qu'il y a aussi des rapports très simples entre les volumes des substances gazeuses et le nombre des molécules simples ou composées qui les forme. L'hypothèse qui se présente la première à cet égard et qui parait même la seule admissible, est de supposer que le nombre des molécules intégrantes dans les gaz quelconques est toujours le même à volume égal ou est toujours proportionnel aux volumes." . . .

"En partant de cette hypothèse on voit qu'on a le moyen de déterminer très aisément les masses relatives des molécules des corps qu'on peut avoir à l'état gazeux."

Further referring to the molecules of elements, he says:

"Les molécules constituantes d'un gaz simple quelconque, c'est-à-dire celles qui s'y tiennent à une distance telle à ne

[1] Abstract of an article entitled "Der Entwicklungsgang der Avogadroschen Theorie," by C. Graebe. Journal für praktische Chemie, N. F., **87**, 145–208 (February, 1913).

pouvoir exercer leur action mutuelle, ne sont pas formées d'un seule molécule élémentaire mais résultent d'un certain nombre de ces molécules réunies en une seule par attraction."

The *molécules constituantes* and *molécules intégrantes* of Avogadro were our molecules, but by *molécules constituantes* he means the molecules of elements and by *molécules intégrantes* he generally means the molecules of compounds, but also molecules of all substances, and later the molecules of elements. The word atom does not occur in Avogadro's articles that appeared from 1811 to 1814.

Graebe considers the recognition of the complexity of the molecules of the elements the greatest scientific contribution of Avogadro. This was entirely new. Dalton had distinctly denied that the same number of smallest particles is contained in the same volume of all gases.

In 1814 Avogadro says:

"Les expériences et analyses qui ont été publiées depuis par plusieurs physiciens et chimistes, et en particulier par MM. Gay-Lussac, Davy et Berzelius, etc., nous permettent maintenant d'étendre nos principes à d'autres substances, sur lesquelles il nous était resté des doutes, ou dont nous n'avons pas parlé."

Attempts by Avogadro to apply the hypothesis to substances which could not be vaporized led to confusion. This made chemists hesitate to accept the hypothesis. Then, too, Avogadro made no experiments.

In 1821 Avogadro published two more articles, one dealing with results which had been obtained by Berzelius, and the other with the question as to the molecular weights of alcohol and ether. These two articles remained unknown to chemists until 1901, when Guareschi called attention to them. It is probable that Berzelius never saw them. Avogadro never tried to impress his views on other chemists. He was very modest. This fact probably explains why he never took exception to the statements of Dumas and Gaudin in regard to the historical development of his hypothesis.

In 1814 appeared the "Lettre de M. Ampère à M. le comte Berthollet sur la détermination des proportions dans lesquelles les corps se combinent d'après le nombre et la disposition respective des molécules dont leurs particules intégrantes sont composées."

By *molécule* Ampère meant our *atom*, and by *particule* our molecule.

Like Avogadro, Ampère starts with Gay-Lussac's law:

"Vous savez que depuis longtemps l'importante découverte de M. Gay-Lussac sur les proportions simples qu'on observe entre les volumes d'un gaz composé et ceux des gaz composants

m'a fait naître l'idée d'une théorie qui explique les faits découverts par cet habile chimiste et les faits analogues observés depuis." . . . "Les particules de tous les gaz, soit simples, soit composées, sont placées à la même distance les unes des autres. Le nombre des particules est dans cette supposition, proportionnel au volume de gaz."

In a footnote he adds: "Depuis la rédaction de mon Mémoire j'ai appris que M. Avogadro avait fait de cette dernière idée la base d'un travail sur les proportions des éléments dans leur combinaisons chimiques."

Ampère's views in regard to the divisibility of the molecules of the elements are the same as Avogadro's.

"Le gaz nitreux (nitric oxide) contenant, par exemple, la moitié de son volume en oxygène et la moitie en azote, il s'ensuit qu'une particule de gaz nitreux est formée par la réunion de la moitié d'une particule d'oxygène et la moitié d'une particule d'azote."

Avogadro and Ampère differ widely in regard to the number of atoms in the molecules of the elements. These complications are probably responsible for the fact that this article was not reproduced in any of the other journals. The greater part of the article is an attempt to determine how the atoms can combine with one another according to the fundamental crystalline forms.

Ampère returned to the subject only once afterwards—eighteen years later. In the later article he defines atom and molecule as they are now defined. He was the first to do this.

From 1811 to 1826 the subject received no further attention. There was not even a reference to the publications of Avogadro and Ampère.

In 1813 Berzelius held that the atomic weights are proportional to the specific gravities in gaseous condition, but he did not extend this idea to compounds and never held that equal volumes of all bodies in gaseous condition contain the same number of molecules.

In 1826 appeared Dumas' *Mémoire sur quelques points de la Théorie atomique*. He refers to Ampère but only secondarily to Avogadro. After this the hypothesis was called Ampère's hypothesis until Cannizzaro set matters straight in 1858. At the end of his article Dumas says:

"Nous sommes bien eloignés de l'époque où la chimie moléculaire pourra se diriger par des règles certaines, malgré les avantages immenses que cette partie de la philosophie naturelle a retirés des travaux de MM. Gay-Lussac, Berzelius, Dulong and Petit, Mitscherlich, ainsi que les vues théoriques de MM. Ampère et Avogadro."

Dumas did not distinguish sharply between atom and molecule. He used the expression "half atom" which led Berzelius to remark:

"Ehemals war es gewöhnlich, dass man eine Hypothese, sobald sie ad absurdum führte, als widerlegt zu betrachten."

In 1832 Dumas found himself in trouble on account of the peculiar results obtained in determining the vapor densities of mercury, phosphorus and sulphur. He halved the atomic weight of mercury and doubled that of phosphorus.

In 1833 Berzelius, in consequence of Dumas' results, abandoned the view that equal volumes of elements in gaseous condition contain the same number of atoms.

In 1833 Gaudin advanced ideas essentially the same as those of Avogadro and Ampère, but he did not mention Avogadro. He held that the molecule of mercury is monatomic, that of phosphorus tetratomic, and that of sulphur hexatomic.

Gay-Lussac and Becquerel made a report to the French Academy upon Gaudin's memoir and in the report occurs this passage:

"Il fait voir que les molécules de vapeur de brome et d'iode sont biatomiques au moins, comme celle du chlore; celle de mercure monoatomique. Le phosphore à l'état de vapeur est tetratomique et la soufre hexatomique."

Berzelius reports in full upon this article in his Jahresbericht. He says: "Das Hauptaxiom ist der von Ampère aufgestellte Satz, dass in allen Gasen der Abstand zwischen den Atomen gleich ist."

Gaudin's article was long ignored or forgotten. In 1838, Avogadro mentions it but does not agree with the author as to the monatomicity, diatomicity, etc., of elementary molecules.

Gaudin's article was helpful in leading to the use of the words atom and molecule in the present sense. In 1858, Cannizzaro confessed his indebtedness to Gaudin in respect to this matter.

In the 30's of the last century vapor-density determinations were used more and more in organic chemistry to control analyses, but they were not taken as decisive. For example, in 1834, Liebig says: "Das specifische Gewicht des Alkoholdampfes kann nicht als Grund für seine Konstitution als ein Oxyd eines anderen Radikals angesehen werden."

Persoz, in 1839, in his "Introduction à l'étude de la chimie moléculaire" used these words:

"Le volume de vapeur que produisent les équivalents de chaque corps en partant de 100 g. d'oxygène pris pour unité est sensiblement égal à 70 litres de vapeur à 0° et 76 cm. de pression

ou à un multiple de ce nombre par 2 ou 4, c'est-à-dire = 140 litres ou 280."

Later Berzelius found that the vapor of acetic acid has a specific gravity corresponding to 3 volumes, i. e., $70 \times 3 = 210$ liters.

In the first volume of his "Handbuch der Chemie" (1843), Gmelin did not specially treat of the hypothesis of Avogadro and Ampère, nor did he mention these investigators. He, however, says:

"Das Gesetz von Berzelius, dass einfache Stoffe im Gaszustand bei gleichem Volum eine gleiche Zahl von Atomen enthalten, ist bereits durch die Erfahrung widerlegt."

In Kopp's "History of Chemistry" (1843–47) no mention is made of Avogadro, and Ampère is referred to only in connection with ammonium and hydrofluoric acid, although Kopp deals fully with the treatise of Dumas on the atomic theory. He doesn't mention the distinction between molecule and atom.

Thirty years later, in his "Entwicklung der Chemie in der neueren Zeit," Kopp gives an explanation of the neglect of Avogadro's treatise. He says chemists were just beginning to familiarize themselves with the relation between the composition of compounds and the relative weights of the smallest particles of the constituents, and the distinction between two kinds of smallest particles seemed rather to complicate than to simplify matters. But still more was the neglect due to the fact that Avogadro put forward his theory without stating a single new fact. And Ampère, who had a high reputation as a mathematician, did not succeed in enlisting adherents to the new ideas.

It appears, indeed, that Ampère's treatises on the molecular hypothesis were not regarded as of much importance even by those who stood in closest relations to him.

At the beginning of the 40's the hypothesis that equal volumes of bodies in the gaseous condition contain an equal number of molecules had been entirely abandoned by chemists. Only Avogadro and Gaudin accepted it but without furnishing further evidence.

Gerhardt recognized its value for the determination of formulas and began a new epoch in the history of Avogadro's theory. The formulas then in use were very complicated. Gerhardt went back to the empirical formulas and found that by using what appeared to be the most reliable atomic weights most formulas must be halved. In 1843 he chose equivalents that gave the formulas HCl, H_2O, NH_3, CO_2, KCl, KHO, SO_4H_2. For the non-metals his atomic weights were the same

as those of Berzelius but with the important difference that he did not assume any double atoms. For the metals his atomic weights were half those of Berzelius. Those of Gerhardt are the same as those now in use with the exception that those of the polyvalent metals are now twice as large as his.

Gerhardt found that the formulas adopted by him for organic compounds whose vapor densities had been determined all corresponded to 2 volumes (i. e., H_2) as is the case with H_2O, CO_2, ClH, and NH_3. In his "Précis de chimie organique" (1844–1845), he says:

"On dit alors que l'équivalent de la substance représente deux volumes de vapeur."

He applied this principle consistently. The only exception was perchloromethyl ether, $(CCl_3)_2O$, which gave a vapor density half as great as was expected. He assumed that it broke down into tetrachloromethane and carbonyl chloride:

$$(CCl_3)_2O = CCl_4 + COCl_2.$$

This was experimentally confirmed by de Soney in 1893.

Gerhardt did not extend his view to the elements. For him the words atom, equivalent, and volume were synonymous. He had not yet accepted the view that the molecules of the elements are divisible.

Laurent was the first to adopt the views of Gerhardt, but he distinguished sharply between atom and molecule, using these words as Ampère and Gaudin had 12 years before. In 1846 Laurent says: "L'atome de Gaudin représente la plus petite partie d'un corps simple qui puisse exister dans une combinaison. Ma molécule représenterait la plus petite quantité d'un corps simple qu'il faut employer pour opérer une combinaison, quantité qui est divisible en deux par l'acte même de la combinaison. Ainsi, Cl peut entrer dans une combinaison; mais pour faire celle-ci, il faut employer Cl_2. J'admets donc, avec M. Ampère, la double décomposition du chlore par hydrogène.

"Si, au lieu de prendre 1 volume pour quelque corps, 2 volumes pour d'autres et 4 volumes pour d'autres, comme ou le fait ordinairement; ou bien, si an lieu de prendre comme M. Gerhardt 1 volume pour les corps simples et 2 volumes pour les corps composés, nous représentons tous les corps, tant simples que composés, par 1 volume nous aurons une notation beaucoup plus régulière.—On a alors:

	1 Molécule
Oxygène O_2	= 200.0 = 1 vol.
Hydrogène H_2	= 12.5 = 1 vol.
Eau H_2O	= 112.5 = 1 vol.
Acide chlorhydrique HCl	= 227.0 = 1 vol."

Laurent uses for the first time such equations as the following:

$$(HH) + (ClCl) = (HCl) + (HCl)$$
$$(HH) + (HH) + (OO) = (HH)O + (HH)O.$$

He also explains the nascent state in the same way as is customary at present.

In 1846, Favre and Silbermann, in studying heat changes in chemical processes, came to the same conclusions as Laurent in regard to complexity of elementary molecules. They found that more heat is evolved when carbon is burned in nitrous oxide than when carbon is burned in oxygen and gave the now commonly accepted explanation that more energy is required to separate the atoms of oxygen from each other than to separate the atom of oxygen from the two atoms of nitrogen contained in the molecule of nitrous oxide.

No notice was taken of these views until 1864, when Würtz in his "Lecons de philosophie chimique" said:

"Rappelous ici que MM. Favre et Silbermann, dans leurs recherches classiques sur les chaleurs produites par les combinaisons chimiques, ont émis les premiers l'idée que la molécule d'oxygène libre est formée de deux atomes."

This is not correct, Avogadro was the first, but Favre and Silbermann furnished experimental evidence in favor of the idea.

Gerhardt and Laurent worked together earnestly, but they were not able to bring about the desired reform in the 40's. At this time nearly all chemists had given up the atomic weights of Berzelius and were using Gmelin's equivalents.

Gerhardt believed that ether was derived from 2 molecules of alcohol but furnished no evidence. Then came (1850) the important work of Williamson that led him to the conclusion that alcohol is water in which half of the hydrogen is replaced by hydrocarbon, and ether is water, in which both atoms of hydrogen are replaced by hydrocarbon,

$$\begin{matrix} H \\ H \end{matrix}O \qquad \begin{matrix} C_2H_5 \\ H \end{matrix}O \qquad \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}O$$

Williamson abandons equivalents and adopts the atomic weights of Gerhardt. He does not, however, mention Avogadro or Ampère.

In the 50's more and more attention was given to the views of Gerhardt, but the abnormal vapor densities gave difficulty and prevented the general adoption of Avogadro's hypothesis.

Bineau (1838, 1839) determined the vapor densities of a

number of ammonium salts and obtained smaller values than were to be expected—for ammonium chloride one-half; for ammonium carbamate one-third. He suggested that these salts may be decomposed by heat.

In 1846 Bineau found different densities for sulphuric acid at different temperatures and offered the same explanation as for ammonium salts.

These ideas were not fruitful at first. Chemists could not believe that hydrochloric acid and ammonia could exist side by side, or sulphuric anhydride and water. Even Gerhardt felt that this view was improbable.

Laurent in his "Méthode de Chimie" (1854) regards the abnormal vapor densities as exceptions. He defended Gerhardt's system of formulas and atomic weights warmly, and Gerhardt accepted Laurent's views regarding the molecules of the elements. Gerhardt even went so far as to speak of free chlorine as chloride of chlorine, and of hydrogen as hydride of hydrogen. He did not make use of the law of Dulong and Petit. All metals correspond to hydrogen; hence the formulas K_2O, Ca_2O, Hg_2O, etc.

In his "Traité de chimie organique" (1853–56) Gerhardt did not use his own atomic weights and only discussed them in the 4th volume. Being asked why he did not use the simpler system, he is said to have replied, "Dann hätte Niemand mein Buch gekauft."

Gerhardt died in 1856, two days before his 40th birthday. The 4th volume of his book was in manuscript and was published later. Laurent died in 1853, a year before his "Méthode de Chimie" appeared.

The work now devolved upon younger chemists—above all Cannizzaro and Kekulé. Both had spent some time in Paris, and later Kekulé went to London, where he became well acquainted with Williamson.

Mendeléeff early recognized the value of the new ideas. In his "Die Grundlagen der Chemie" (German edition, 1891) he speaks of the molecular hypothesis as the hypothesis of Avogadro and Gerhardt.

In 1857 Clausius used these words: "In dem ich nach einem gemeinsamen Gesetze für die Volumverhältnisse der Gase suchte, bin ich endlich bei folgender Ansicht, als der wahrscheinlichsten stehen geblieben, welche ich dem wissenschaftlichen Publikum wenigstens als eine Hypothese, die der weiteren Prüfung wert ist, glaube vorlegen zu dürfen. Ich nehme an, dass die Kraft, welche die Entstehung chemischen Verbindungen verursacht und wahrscheinlich in einer Art von Polarität der Atome besteht, auch schon in den einfachen

Stoffen wirksam ist, und dass auch in diesen mehrere Atome zu einem Molekül verbunden sind. Der einfachste und daher wahrscheinlichste Fall würde der sein, dass zwei Atome ein Molekül bilden."

Verdet called attention to the fact that these ideas of Clausius were not new, but that Laurent and Gerhardt had advanced similar views. Clausius afterwards acknowledged the justice of Verdet's criticism.

In 1857 appeared an important article by Sainte-Claire Deville entitled "Sur la dissociation ou la décomposition spontanée des corps sous l'influence de la chaleur." Deville always remained an opponent of Avogadro's theory but furnished some of the best evidence in its support.

Cannizzaro at once recognized the value of this evidence. He says:

"Ich glaube, dass es keine Ausnahme von dem allgemeinen Gesetz gibt, nach welchem gleiche Volum gasförmiger Körper eine gleiche Anzahl Moleküle enthalten, und dass die scheinbaren Anomalien bei einer strengen Prüfung verschwinden werden."

Kopp (1858), after the appearance of Deville's article, accepts the explanation of abnormal vapor densities suggested by it.

Kekulé (1858) also accepts the same explanation but he does not base his conclusions upon Deville's results. He is discussing Baeyer's discovery of the decomposition of cacodyl trichloride by heat.

Cannizzaro went farther than Kopp or Kekulé. He says Avogadro's hypothesis is in harmony with all facts. He expresses himself even more strongly in his "Sunto di un corso di filosofia chimica fatto nelle R. Università di Genova" (1858). This is the real turning point. He puts the main point very clearly.

"Ich glaube, dass die in dem letzten Jahren gemachten Fortschritte der Wissenschaft die Hypothese von Avogadro, Ampère und Dumas über die ähnliche Beschaffenheit im Gaszustand bestätigen, dass heist, dass gleiche Volum der selben, mögen sie einfach oder zusammengesetzt sein, eine gleiche Anzahl von Molekülen enthalten, aber nicht eine gleiche Anzahl von Atomen. . . . . In meiner ersten Vorlesung begann ich zu zeigen wie aus der Betrachtung der physikalischen Eigenschaften der Gase und des Gay-Lussac'schen Gesetzes über das Verhältniss des Volumens der Verbindungen und ihre Bestandtheile jene Hypothese fast von selbst entsprungen ist, welche zuerst von Avogadro und kurz nachher von Ampère verkündigt wurde."

This is the first statement to the effect that Avogadro was the first to suggest this hypothesis. The fact had been forgotten by his fellow-countrymen. It was not mentioned in an article which appeared in the Nuovo Cimento of Matteuci and Piria in 1856, at the time of Avogadro's death, nor in an article by Piria (1857), in which the author accepts the view of Gerhardt that the molecules of the elements consist of 2 atoms each.

Cannizzaro calls the molecular theory generally the hypothesis (sometimes the theory) of Avogadro and Ampère.

Cannizzaro proposed to select atomic weights of the metals to conform to the law of Dulong and Petit.

Kekulé, in his "Lehrbuch der organischen Chemie," the introduction to which appeared in 1859, bases his reasoning largely upon chemical considerations as did Gerhardt and Laurent. He reaches the conclusion "dass die chemischen Moleküle mit den physikalischen Gasmolekülen indentisch sind," and therefore that "gleiche Volume gasförmiger Körper eine gleiche Anzahl chemischer Moleküle enthalten."

Cannizzaro's "Sunto" was not republished in any journal, and the Jahresbericht gave only an inadequate account of it. Therefore it remained practically unknown. Then came the Congress of Chemists at Carlsruhe in 1860, which was due largely to the initiative of Kekulé. Here Cannizzaro played a leading rôle and made a strong impression. He proposed to adopt Gerhardt's system and to make the necessary changes in the atomic weights of a number of metals.

Kekulé and Strecker supported him but no decision was reached. One thing came out clearly—that Avogadro was the first to advance the hypothesis which was still frequently attributed to Ampère. At the close of the meetings Cannizzaro distributed reprints of his "Sunto." Later Lothar Meyer told of the effect upon himself of the careful study of this "Sunto." As he says: "Es fiel mir die Schuppen von den Augen, die Zweifel schwanden und das Gefühl ruhigster Sicherheit trat an ihre Stelle. Wenn ich einige Jahre später etwas für die Klärung der Sachlage und die Beruhigung der erhitzten Gemüter habe beitragen können, so ist das zu einem nicht un wesentlichen Teil der Schrift Cannizzaro's zu danken."

Kekulé in the last number (Lieferung) of the first volume of his "Lehrbuch" (1861) changed the atomic weights of mercury, zinc, tin, and lead. He doubled them as suggested by Cannizzaro.

Kopp, in the second edition of his "Theoretische Chemie" (1863), gives the newer views concerning molecular weights,

atomic weights and equivalents according to Avogadro's hypothesis and the law of Dulong and Petit.

Lothar Meyer treats fully of Avogadro's hypothesis in his "Die modernen Theorien der Chemie" (1864). In the later editions he uses the expression Avogadro's rule.

Würtz, in his "Leçons de Philosophie chimique" (1864), speaks of the law of Ampère; in later publications of the law or theory of Avogadro and of Ampère; and finally he leaves Ampère's name off entirely.

In the second edition of his "Die modernen Theorien der Chemie" (1872) Lothar Meyer says:

"Seit die Schlussbetrachtungen zur ersten Auflage geschrieben wurden, hat die Entwicklung der theoretischen Chemie einen wesentlichen Schritt vowärts getan. Die damals noch bestrittenen oder doch nicht ausdrücklich anerkannten Hypothesen von Avogadro und von Dulong und Petit sind als die Grundlagen der Atomgewichtsbestimmung allgemein anerkannt worden; die Gmelinschen sog. Äquivalente sind aus der Literatur verschwunden."

Up to 1863 the "Jahresbericht" used only equivalents, then equivalents and atomic weights according to the author quoted; after 1873 only the new atomic weights.

In spite of all, the hypothesis of Avogadro still remained a subject of controversy, but the day was won. Würtz, in 1877, came to the defense, but felt that the hypothesis no longer needed a defender. He writes to van't Hoff in 1877:

"Avez-vons suivi dans le Compte rendu ma discussion avec Berthelot et Deville et n'est-il pas triste d'avoir à soutenir de pareils combats pour une cause gagnée depuis 20 ans?"

The discussion continued until 1880. Berthelot and Deville never accepted the hypothesis but they were without followers.

I. R.

REVIEWS

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S., Emeritus Professor of Chemistry, Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. Revised and enlarged edition in five volumes. Vol. IV, Oilstone to Soda Nitre. With illustrations. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1913. pp. viii + 727. Price, $13.50.

Reviews of previous volumes of this new edition have appeared in these columns,[1] and it is very satisfying to find this fourth volume appearing with the promptness promised in

[1] This Journal, **48**, 191, 259; **49**, 257.

the original prospectus, i. e., that the entire set should be complete in two years. To this volume forty-nine contributors have supplied the articles, some of which are quite long. About one hundred and fifty are new topics not found in the old edition, the more important being the following: Oxydases; Ozonides; Palm Kernel Oil; Palm Oil; Percarbonates; Perfumes (Synthetic); Phenylacetic Acid; Phenylglycine; Phytosterol; Pitchblende; Plant-Sprays; Polarimetry; Polonium; Propiolic Compounds; Propyl; Proteins; Ptomaines; Purpurogallin; Pyrazoline; Pyrimidines; Pyrites; Pyrometry; Pyronine Colors; Quebracho Colorado; Racemism; Radioactivity; Radium; Refractometer; Refrigerating and Ice-Making; Rhodinol; Rosinduline; Safrole; Samarium; Santalene; Santalol; Saponification; Scandium; Sewage; Silk, Artificial; Smoke and Smoke Prevention.

About fifty articles from the old edition have been entirely rewritten and materially enlarged; among these may be noted: Oxalic Acid; Oxazine Coloring Matters; Oxygen; Ozone; Parchment Paper; Pepper; Persian Berries; Petroleum; Phenacetin; Phenanthrene; Photography; Phthalic Acid; Picric Acid; Pottery and Porcelain; Praseodymium; Primuline Derivatives; Purple of the Ancients; Pyrazolines; Pyrogallol; Quartz; Quinoline; Quinones; Quinone-oxime Dyes; Resins; Rubber; Rubidium; Rum; Rust; Salicylic Acid; Selenium; Silicon; Silver; Silvering.

The references cited in several cases show that the articles have been brought up to 1912. Many new references to mineral products used as raw materials, and to vegetable products such as fruits and drugs, have been included in this edition.

The topic of Oxygen is considered in two sections: the chemical methods of production, and the mechanical and electrical processes. Of the chemical methods, the manganese dioxide-potassium chlorate process and the Brin barium oxide process are still in use in a few places. But the mechanical process from liquid air, and the electrolysis of water, are now more important, although the electrolytic methods depend upon a market for the hydrogen, in order to compete with the liquid-air method. Both of these methods are well illustrated.

The industrial preparation and utilization of Ozone is well, though briefly, treated, and the several types of commercial ozonizers described in short paragraphs on each. The most important use for ozone is in purifying water for domestic purposes, and large scale installations at St. Petersburg, Florence, Nice and Philadelphia are cited. The cost of purifying water is also considered. The use of ozone for purifying the air in

buildings and enclosed spaces, for bleaching various organic substances, and for sterilizing is also mentioned. Ozonides, the derivatives produced by the action of ozone on unsaturated organic compounds, fill three pages of text. Oxydases fill a page and a half, in which are several citations from the publications of Kastle and Loew in this country.

Synthetic Perfumes are treated in a readable article of about eight pages. It is stated that nearly all flower perfumes can be imitated, more or less successfully, but in the case of violet, and rose oil, the imitations do not approach the natural substance in fragrance. The relation between constitution and smell is discussed briefly. A list of substances used in compounding perfumes, with their constitutional formulae when known, their chemical properties, and methods of preparation or isolation from natural sources, is included. Also the constituents of the more important blends found in the market.

Under American Petroleum is found the first article, in this volume, by an American authority, Dr. S. P. Sadtler, of Philadelphia, who contributes a digest of the industry as at present conducted in this country. A longer article by Sir Boverton Redwood covers the industry as developed in other parts of the world, and especially a full discussion of the testing of petroleum oils.

Plant-Sprays are considered under the three classes, solids, liquids and gases, spraying being used in its widest sense as the application of these materials to plants to rid them of insects, fungoid parasites and other matters interfering with healthy growth. The methods of preparation and the application and properties of the more important sprays and washes are suitably discussed.

In the extensive article on Polarimetry, the qualitative and quantitative examination of optically active substances, the effect of asymmetric atoms on optical activity, Walden's inversion, the general relations of rotation and chemical constitution, the influence of changes of temperature and pressure on rotation, and the rotation of active salts in solution are fully treated. The optical principles of the Nicol prism and its various modifications, with descriptions of the polarimeters of Mitscherlich, Laurent, Lippich, and the modern Schmidt and Haensch instrument, are included.

In the article on Proteins, the labors of Emil Fischer and his students are well outlined. The reactions, physical properties, classification, separation and identification of the proteins are briefly considered. Then follow paragraphs upon the conjugated proteins and the hydrolysis of proteins by enzymes.

Pyrometery is set forth in an illustrated article of about eight pages. The various methods and instruments employed in high temperature determinations are well described; a bibliography of the subject is also included.

In the article on Quartz is a short paragraph upon its use for making fused silica ware, now so important in chemical industry. A somewhat more lengthy treatment of this subject is, however, found in the topic Silicon and a cross-reference here would be useful.

Quinones furnish one of the longest articles in this volume, profusely illustrated with structural formulae and equations, and interspersed with copious references to original literature.

The interesting developments of Radioactivity, beginning with Becquerel's work in 1896 and extending to the very recent papers by Rutherford and others, fill about ten pages.

Refractometers are illustrated by descriptions of the instruments of Pulfrich, of Abbe, the butter instrument, and the dipping instrument. The conditions essential for satisfactory work in investigations with these instruments are shown.

The article on Refrigerating and Ice-Making Machinery consists mainly of a theoretical consideration of the principles upon which are based the two general types of machines—those employing the expansion of compressed air and those depending on the abstraction of heat by evaporation of a volatile liquid. A number of industrial applications of refrigeration are cited, but few details of practice are given.

Rubber is the title which replaces *Caoutchouc* or *India-rubber* of the old edition. The constitution of rubber and its synthetic preparation by condensation of isoprene is referred to very briefly, but is admittedly not a commercial possibility as yet. The manufacture of rubber goods is described, with illustrations of some of the machinery.

Under Rust are outlined the various theories as to the causes and phenomena of the process, with reference to the older work of Crace Calvert and Crum Brown, and the recent investigations of Whitney, Dunstan, Moody, Friend, Cushman, Walker, and others. The electrochemical theory is now generally accepted. Consideration is given to the influences of physical and chemical heterogeneity, and of dissolved substances in the rusting process; also in the prevention of rust.

Saponification is discussed in its wider sense, meaning the resolution of oils and fats into glycerol and fatty acids, or their salts; the term is synonymous with "hydrolysis." After consideration of the general methods of saponification, the author takes up the Twitchell process, employing sulpho-aromatic compounds, but he does not feel justified in making detailed

statements as to the mode of preparation of the "saponifier," owing to the secrecy imposed upon licencees using the process. A very good outline of the method of Connstein, Hoyer, and Wartenberg, using the fat-splitting enzyme, is included.

The very important topic of Sewage is condensed into about seven pages. Reference to the work of the Massachusetts Board of Health in connection with these problems, and tabulated data from the Reports of the Royal Commission (upon River Pollution?) are included in the article.

Artificial Silk is briefly treated in about four pages. The various processes of Chardonnet, Pauly, and others similar to them, and those employing cellulose thiocarbonate, are described; also some of the details of the apparatus employed. Various tests, and the properties of the several kinds of fiber, are included.

Smoke and Smoke Prevention fill only five pages, but the subject is considered chiefly from the point of view of the domestic open-grate fire—a mode of heating far more general in Great Britain than in this country. It is stated that manufacturers have demonstrated the possibility of smokeless coal combustion, through improvements in furnace construction, and by mechanical stoking, but no description is given of any of these devices. The chief remedies recommended for the smoke nuisance are the use of coke or anthracite or fuel gas.

Comparatively few of the more striking new developments in chemical industry happen to fall within the alphabetical limits of this volume, and some of the articles seem to give the impression that space limitations have hampered the writers more or less; yet the book as a whole maintains the standard of its predecessors; in its make-up and typography it is very satisfactory.

F. H. THORP

ACTION OF THE SALTS IN ALKALI WATER AND SEA WATER ON CEMENTS. By P. H. BATES, Chemist, A. J. PHILLIPS, Assistant Chemist, and RUDOLPH J. WIG, Associate Engineer Physicist, Bureau of Standards. Technologic Papers of the Bureau of Standards, Department of Commerce, No. 12 (November, 1912). Washington: Government Printing Office. pp. 157.

That concrete is subject under certain conditions to disintegration by sea water has been known for many years but just what these conditions might be has long baffled investigators. There are many instances where concrete structures have successfully withstood the action of sea water for many years and the closest inspection fails to reveal any signs of disintegration. This is true not only of concrete which is constantly submerged in sea water but also of concrete surfaces which are alternately submerged and exposed by the tides.

On the other hand, we have many instances where concrete has been seriously affected by the action of sea water, which action at times has caused complete disintegration. Laboratory tests on the action of artificial sea water on concretes seem to uniformly prove that concrete is subject to more or less rapid and complete disintegration and that this effect is apparently caused by the action of magnesium sulphate on the lime and alumina of the cement, there being formed hydrated magnesia and calcium sulpho-aluminate, both of which, because of their high content of water of crystallization, have a greater volume than the compounds which they replace.

The reclamation of the vast arid areas of our country by irrigation has called for the varied and extensive application of concrete. It was soon noticed that the concrete in many instances was being seriously affected, presumably by the alkali which was present in the soil in large percentage. The Agricultural Departments of the states of Colorado and Montana conducted extensive investigations along this line and accumulated much valuable data. As much of this irrigational work is being done under direct supervision of the Government, it was considered timely to inaugurate an extensive investigation. This was first conducted by the Structural Materials Laboratory at St. Louis and later undertaken by the Bureau of Standards.

This is the first report made on the results obtained both in the laboratory and under actual or field conditions, the latter being conducted at Atlantic City. In the laboratory experiments cement mortars and concretes of various compositions were exposed to the action of solutions of many alkaline salts and combinations of these salts and the chemical and physical effects observed. The conclusions drawn from these experiments may be briefly stated as follows: Cement mortars and concretes are disintegrated by the mechanical action of almost any salt in its pores if a sufficient amount of it is allowed to accumulate so that the crystals formed will exert an expansive action. This is not only true of concretes but porous stone, brick and other structural materials are disintegrated in the same manner. While in the laboratory mortars and concretes are disintegrated by the chemical action of various sulphate and chloride solutions, field tests show that such action is very slight and it is assumed that the concrete is protected by an impervious skin of calcium carbonate. Properly proportioned Portland cement concrete, when totally immersed, is apparently not decomposed by the chemical action of sea water. Natural slag and other cements tested in concretes showed normal increase in strength with age in sea water. There is no apparent relation between the chemical composi-

tion of a cement and the rapidity with which it reacts with sea water when brought into immediate contact. It is stated that tricalcium sulpho-aluminate could not be formed. While the sulphates are the most active constituents of sea water taken up by cement and the presence of chlorides accelerates their action, no definite sulphate compound could be established. Metal reinforcement is not subject to disintegration if embedded to a depth of 2 inches or over in well-made concrete. As this series of experiments extended over a period of only three and one-half years, these conclusions must be regarded more as observations than as definite conclusions. C. N. WILEY

ZINK UND CADMIUM UND IHRE GEWINNUNG AUS ERZEN UND NEBENPRODUKTEN. Von R. G. MAX LIEBIG, Hüttendirektor a. D. Mit 205 Figuren im Text und auf 10 Tafeln, sowie einem Titelbilde. Chemische Technologie in Einzeldarstellungen. Herausgeber: PROF. DR. FERD. FISCHER, Göttingen-Hamburg. Spezielle Chemische Technologie. Leipzig: Verlag von Otto Spamer. 1913. S. xvi + 598. Preis: geh., M. 30.00; geb., M. 32.00.

Until the appearance of the present volume, there existed only two treatises on the metallurgy of zinc, one by W. R. Ingalls (New York, 1903), and the other by Lodin (Paris, 1905). It has always been surprising that the Germans, who have books on most subjects, should not have issued a volume treating of zinc, especially when it is remembered that until 1906 Germany was the leading producer of this metal. The reason for this lies probably in the unfortunate custom of most zinc smelteries of not giving out information of prevailing practice. This prevents the zinc metallurgist from undertaking the task of preparing a treatise; and without considerable practical experience with the metal it is very difficult even for the well-versed metallurgist to sift the large amount of heterogeneous matter found in technical periodicals.

The author, retired from practical work, adds now to his acknowledged high rank as zinc metallurgist the merit of having written a masterly work upon the metal to which he had devoted his technical activity.

The subject is treated in ten chapters. At first are discussed the ores of zinc and cadmium, and the modes of purchasing and of sampling; then follows a brief review of the properties of zinc and its compounds. This introductory part closes with a description of work in the chemical laboratory, an appendix giving numerous chemical analyses of ores, intermediary and final products.

The extraction of zinc from its ores by smelting is treated historically under the usual five headings of English, Carinthian, Silesian, Belgian and Rhenish modes of operating; in an

appendix are given other methods which do not fit into the general classification; the whole is introduced by a history of the metal. By the historical method of presentation the evolution of the different types of furnaces is brought out clearly. In Chapter V is taken up the calcining and roasting of ores; then follow the manufacture of clay vessels, the preparation of charges, the chemistry of reduction, the condensation of zinc vapor, details of the construction of some parts of the furnaces, ventilation of furnace room, removal of residues, and lastly, the refining of crude zinc. Chapter VI discusses briefly the metallurgy of cadmium, and Chapter VII the preparation of zinc white. The uses of zinc and its oxides and of cadmium receive some consideration. The different non-electric and electric smelting methods proposed are reviewed in Chapter IX. This is followed by a similar treatment of the numerous electrolytic processes which have been advocated, tested and mostly abandoned. A few statistical notes close the last chapter.

This general statement gives an idea of the ground covered; it is not desirable to go into details, nor is it necessary, as the whole has received a careful treatment from the chemical, mechanical, technical and economic points of view; everywhere we see theory and practice well combined.

As far as the contents are concerned, we have a great book. It seems a pity that everything is not perfect. There is, in the first place, no index. The author states that he did not provide any, as it would have had to be very long to be at all adequate; he has therefore elaborated the table of contents, making this do duty for an index. An index of this book would have taken up from 20 to 30 two-column pages. Considering that a book of 598 pages, $9^1/_4 \times 6^1/_2$ inches, is $2^3/_4$ inches thick, and has the cumbersome weight of five pounds, the hesitation of the author to increase the bulk finds an explanation. It is hoped that with the first reprint the publishers will use a thinner paper and thus reduce this thickness and weight of the book, and leave room for an index.

H. O. HOFMAN

INDUSTRIAL CHEMISTRY. A Manual for the Student and Manufacturer. Edited by ALLEN ROGERS, in Charge of Industrial Chemistry, Pratt Institute, Brooklyn, New York, and ALFRED B. AUBERT, formerly Professor of Chemistry, University of Maine, with Thirty-four Collaborators. 340 illustrations. New York: D. Van Nostrand Co. 1912. pp. xiv + 854. Price, $5.00.

To attempt to cover the field of Industrial Chemistry in a single volume is a heroic undertaking. The ideal method, without question, is to call upon specialists for the discussion

of various topics, but the task is not lightened thereby. Because an author is competent to write upon a given subject, it does not follow that he is especially qualified for sorting out and pruning down the material to meet a specified space. It is, moreover, difficult to prepare material for the student who may be looking for a statement of general principles and at the same time meet the needs of the manufacturer who may desire specific details in his own particular line. In view of these facts, it may be fairly said that the volume in hand has been compiled with a degree of success which on the whole must be considered noteworthy. It must be remembered that the manufacturer in his own line will be reinforced with the special literature pertaining to his subjects, but the interrelation of chemical processes makes it desirable to have at hand a treatise which will give the descriptive matter of associated topics in sufficient detail for reference, even by the manufacturer.

Metallurgical subjects have been eliminated with one exception, that of the Manufacture of Iron and Steel. But having broken over the rule to this extent, the question may fairly be asked whether it would not have been equally justifiable to include a paper on alloys, bearing metals, etc. With the material on the Manufacture of Iron and Steel, it is commendable that a most excellent bibliography is given at the end of the paper. This feature is the more conspicuous for the reason that it is absent from many of the other discussions. In a book of this character, where the various topics must be treated in such a meager manner, it would seem that the greatest service could be rendered by listing the very best references obtainable. The list at the end of the topic on Iron and Steel is an excellent example of what one might wish to see at the end of other papers.

As an illustration of what seems to be a poor balance of treatment, considering the importance of the subjects, the fact is noted that the topic of Fuels is given 22 pages, 5 pages of which are taken up with a discussion of the manufacture of coal gas, water gas, and the regenerative furnace, topics which are treated more or less fully under other headings. Again, under the topic of Fuels, there are discussed such topics as Pyrometry, Calorimetry, and the Coking of Coal by both the bee-hive and the by-product ovens; so that the data on Fuels and the problems of combustion are meager. In contrast with this, it is noted that the topic of Producer Gas alone occupies 22 pages. The illustrative table of type fuels on page 76 is rather seriously in error. The analysis seems to have been taken from artificially air-dried samples. The coals of Illinois, for example, are shown as having 4 and 7 per cent. of moisture, and the fac-

tor for volatile combustible is 28.86 per cent., which would seem to represent a type of coal not found in that state. On page 72 the nitrogen factor for pine of 6 per cent. is, of course, a typographical error.

It might be a question whether more space might not have been given to the subject of Glycerine, 1 page, even though it might have been found necessary to cut down the topic of Laundering, 13 pages. Doubtless, the editors found it, in many instances, less embarrassing to cut down their own contributions than to control the size and scope of those of their collaborators. While it is easy to point out many instances where the material might have been presented differently, the work on the whole is admirably presented and is especially to be commended for its fresh and up-to-date treatment of processes as they are carried out in this country. The industrial wealth in many lines in our own country and the desirability of setting forth the development of processes which have resulted here instead of copying old-time and abandoned methods, even though classical in character, must be put down to the credit of this work.

S. W. PARR

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Vol. VII. Fourth edition, entirely rewritten. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, S.B. Philadelphia: P. Blakiston's Son & Co. 1913. pp. ix + 563. Price, $5.00.

Seventeen years have elapsed since the last edition of the volume under consideration appeared and the present revision is, to say the least, timely.

Volume VII deals with Vegetable Alkaloids (in this respect being a continuation of Volume VI), Glucosides, Non-Glucosidal Bitter Principles, Animal Bases, Ptomaines or Putrefactive Bases, Animal Acids, Lactic Acid and Cyanogen and Its Derivatives, in the order named. Each chapter has been written by a contributor especially qualified to treat the subject under consideration. The classification in some places seems to be somewhat incongruous, but this is explained by a statement in the preface by the editors that "In order to interfere as little as possible with the original plan of the work the old arrangement has been retained so far as this has been found practicable. In retaining the old classification the editors have specially considered those chemists who, having become habituated to the order in former editions, look to find information in the new work in much the same position as in the old one." In spite of this explanation, it would seem to have been better to have included the chapter on Vegetable Alkaloids in Volume VI. It is unusual and unnatural to dis-

cuss, in a work of eight volumes, alkaloids, lactic acid and cyanogen and its derivatives in the same volume.

In the main, the revision has been most painstaking and thorough and the subject matter has been brought well up to date. The subjects treated in the volume in hand form a class than which there is probably none more difficult from the standpoint of analysis and quantitative determination and therefore the editors and publishers are to be congratulated upon the completeness of the work. There are only a few instances where quantitative methods have been overlooked which should have been included, and these omissions are probably due to the fact that such methods are scattered most widely and frequently in the most obscure and difficultly accessible chemical and pharmaceutical literature. One notable example is the method given on page 155 for the determination of santonin in worm-seed or *Santonica*. The method given was published in 1899 and has undoubtedly proved very unsatisfactory in the hands of all those who have attempted to use it. In September, 1912, there was published by Fromme in the *Jahresbericht* of Caesar & Loretz of Hamburg a method for the determination of santonin in *Santonica* which is very satisfactory indeed.

It is unfortunate that the present volume cannot include the methods for the determination of alkaloids which will be contained in the forthcoming revision of the United States Pharmacopoeia and which will in most instances be different from those contained in the volume under review, but as the Pharmacopoeia will not appear for at least another year, it would perhaps be asking too much to delay the publication of the present volume until that time.

The paper, typography and binding of the book are excellent and it is to be highly recommended to all analytical and commercial chemists as a valuable working adjunct and practically a *vade mecum*.

CHARLES E. CASPARI

PHYSIKALISCHE CHEMIE DER HOMOGENEN UND HETEROGENEN GASREAKTIONEN, unter besonderer Berucksichtigung der Strahlungs- und Quantenlehre, sowie des Nernstschen Theorems. Von DR. KARL JELLINEK, Privatdozent an der Kgl. Technischen Hochschule Danzig. Mit 221 Abbildungen im Text und 104 Tabellen. Leipzig: Verlag von S. Hirzel. 1913. S. xiv + 844. Preis: geh., M. 30.00; geb., M. 32.50.

This extensive treatise doubtless began, as the title indicates, with a study of the statics and kinetics of gas reactions; but as the author became interested in the various recent developments of Physics and Chemistry these have been successively included. This gives to the table of contents the appearance of extraordinary heterogeneity. The first three chapters

deal solely with the laws of thermodynamics, excepting in so far as the so-called Nernst "Theorem" is introduced. The fourth chapter develops the theory of radiation; Kirchoff's law, Maxwell's electromagnetic equations, pressure of radiation, the law of Stefan and Boltzmann, the law of Wien, and finally the Blanck radiation formula with a discussion of elementary oscillators. In this chapter the author follows very closely the treatment given by Planck in his "Vorlesungen über die Theorie der Wärmestrahlung." Continuing the discussion of the quantum theory, the fifth chapter deals with the specific heats of solids and the equations of Einstein, Nernst and Lindemann, the specific heats of gases, and the numerous chemical constants that have been related by various authors to the fundamental quantity h of the quantum theory.

Here ends the theoretical part, and next come chapters devoted to experiments on radiant heat and the proper oscillations within the molecule; the measurement of temperature and of thermal quantities; and at last a chapter upon equilibrium in gas reactions, where the author follows the methods of Haber's book, but without displaying Haber's unusual critical acumen. In fact, a number of very doubtful experimental results, obtained in some cases with the express intention of verifying a predetermined theory (for example, the hydrocyanic acid equilibrium, p. 664), the author accepts at their face value. The remaining chapters of the book deal with the kinetics of gas reactions and with the various chemical processes occasioned by ions, silent electric discharge and ions.

The book is written with intelligence but apparently without inspiration. In spite of enormous padding the volume is sufficiently well indexed to be convenient for reference. To a student interested in the quantum theory, as every chemist and physicist is bound to be ultimately, certain chapters offer a very complete bibliography and résumé of the scattered articles which have appeared during the past few years in this important field.

GILBERT N. LEWIS